magnetochemistry

Perspective article

Molecular Spins in the context of Quantum Technologies.

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Abstract: Molecular spins have shown interesting quantum features which make them potential candidates for the implementation of quantum information processing. New challenges related to possible applications in broader class of quantum technologies are currently under discussion. Here, we revisit some key features trying to learn something from experiences in near fields.

Keywords: Molecular NanoMagnets; Quantum Technologies.

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1. Introduction

Quantum Computing (QC) is one of the Quantum Technologies (QT) [1] that aims at exploiting genuine quantum features of systems and devices. QC was envisaged in early Eighties by Richard Feynman and other pioneers and since then other possible applications of quantum systems became feasible also thanks to technological progress. Among QTs, quantum-communications, sensing, cryptography and metrology are now attracting much interest. Besides the discreteness of energy levels, the possibility to create and maintain superposition of states and quantum correlation (entanglement) are considered two of the main features of quantum systems that do not exist in the classical world. Quantum systems such as photons, cold atoms, spin impurities in solids, semiconducting and superconducting devices have been intensively studied in the last decades and several applications based on these systems are in rapid development and some of these already appeared in the market.

Different spins centers in solid state have been -and they currently are- intensively studied for potential applications: spin impurities in Si have been studied and proposed for qubit encoding [2]; Nitrogen Vacancies (NV) centers, as well as other colour centers in diamond or SiC, are now attracting much interest for their potentialities as atomic scale sensors, besides the possibility to use them as hardware for QC [3]. In spite of different preparation technologies, experiments (eg. manipulation and read out of spin) and modeling (eg. spin dynamics, source of decoherence, spin entanglement etc.) all these spins systems obviously share many analogies, thus we can probably learn something by comparing the properties of molecular spins to those of other spin systems. This is intended to be the main stream of this perspective article. We shall focus on three main trends in the field: coherent manipulation of spin ensembles; molecular quantum spintronics and perspective to embed (molecular) spins in quantum circuits.

2. Coherent spin dynamics of spin ensembles.

Quantum effects in molecular spin systems have been explored in the last two decades. The first milestone was the discovery of quantum tunneling of the magnetization in Nineties that demonstrated that molecular spins are real systems on which quantum effects can be controlled and studied in laboratory conditions [4]. Next challenge was to control the dynamics of molecular spins. Molecules with low spin ground state (ideally S=1/2) well isolated by excited states are prototypical cases for this type of study [5] and long-lived coherent oscillations between two spin states is target experiment that can be performed by pulsed Electron Spin Resonance (ESR) techniques. The understanding and control of decoherence mechanisms are of fundamental importance for the dynamics of spins in solid state environment. Thus, in the last decade there has been an intense activity in searching molecular spin systems with improved performances, more specifically with the longer relaxation (T_1) and dephasing (T_2) times, as discussed in previous reviews [6, 7] and themed issues of specialized Journals and book series [8, 9, 10]. Inter-molecular interactions are, in general, detrimental, thus working with spin ensembles diluted in non magnetic matrix is mandatory. In this way, coherent spin oscillations were soon observed in low-spin Cr_7Ni rings [11] and V_{15} [12] at liquid He temperature.

Most of the solid state hardware for quantum technology works at cryogenic temperatures yet this limits all of them to niche applications and increasing the working temperature –and reducing the use of magnetic field- is certainly appealing in view of widely spread applications. Working at 2K instead of 20mK is a gain of two orders of magnitude in temperature and this allows to avoid the use of dilution refrigerators. Working at 20K will allow a gain of another order of magnitude and, for instance, the use of closed cycle refrigerators that can be developed even on one chip. At 80K we may use liquid nitrogen and room temperature operation will open to much broader class of applications. A first breakthrough along this line was obtained with the report of persistence of long T_2 up to 100K in commercial CuPc derivative [13]. This result was followed by rational design of mononuclear derivatives for which T_2 was further improved [14, 15, 16]. The relevant figure of merit here is the ratio between the manipulation time and the spin coherence time. Since for typical pulsed ESR set up the time to manipulate an electron spin is about 10ns, both T_1 and T_2 need to be much longer in order to observe coherent spin oscillations and, possibly to perform some error corrections. As a matter of facts, Rabi oscillations at room temperature have been recently reported in VOPc [17]. These results represent an important milestone for molecular magnetism.

In ref.13 one can find a direct comparison of relevant coherence time measured at different temperatures in different spin systems. Yet, care should be taken in making direct comparison since data should be taken in similar conditions and experiments. One relevant point is the dependence of decoherence times of spin defects on the depth of impurity in the solid. For instance, it is well documented that T_1 and T_2 decrease for shallow impurities in both Si and diamond and they dramatically drop when spin is closer than 5nm to the surface. For instance, fig.1 (from ref.18) shows that both T_1 and T_2 drop below 100μs for NV positioned less than 10nm from the diamond surface. Interestingly, the coordination of the spin center is not altered but the shallow defects were demonstrated to be sensitive to both the magnetic and the electric [19] noise on the diamond surface. This should draw our attention to control the environment of our spin: if impurities are diluted in nuclear free environment, magnetic noise can be drastically reduced. Same attention should be taken to reduce (electrical) noise produced by local vibrations. From this point view, the seminal work reported in ref.20 demonstrated that molecular engineering can be a powerful tool to control the closest environment of the spin. On the other hand, if we need to expose spins to an external environment, such as a biological system or an electronic circuit, the ligand shell may, in some ways, protect or, at least, define the closest surrounding around the sensitive spin.

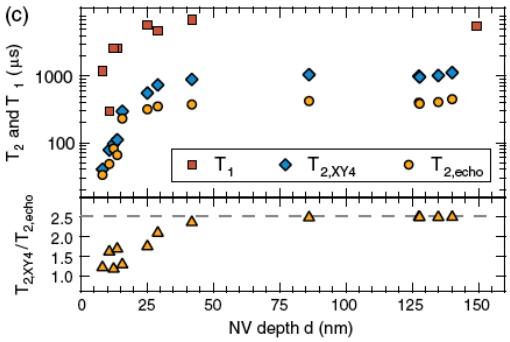

figure 1 Coherence time T_2 and relaxation time T_1 as a function of the NV depth in diamond. The plot shows strong suppression of coherence for shallow NV centres. The lower panel shows $T_{2;XY4}$=T_{2echo} ratio that is reduced as well with decreased depth, also indicating that dynamical decoupling with N=4 pulses is less efficient for shallower NVs. (Reproduced from ref.18 with permission from Americal Physical Society)

In view of possible applications for which spins need to be embedded in external environment, the next challenge seems to be the consolidation of performances with an overall (chemical, structural) robustness of the molecules in different working conditions. To this end, tests on isolated molecules on surfaces or under different stimuli or thermal cycling need to be performed. Important achievements have done by studying isolated molecules on surfaces by different techniques such as STM or X-ray spectroscopies. Not all, but few molecules resulted to be robust enough to substantially maintain their (static) magnetic features when dispersed. However subtle effects may occur when the environment change and these need to be carefully checked case by case [21]. We expect that different molecules can be designed for specific ambient/applications, thus, for instance, molecules with external organic ligand and specific linkers will be more suitable for biological applications; molecules that can be sublimed and with linkers designed to graphitic or Si surfaces will better work embedded in electronic circuits; while molecules with robust periphery (eg. oxygen ligand) can be possible applied in ambient (air) conditions.

Quantum computation may require the implementation of quantum gates [22]. A Universal scheme for computation that, in principle, solves a broad class of computational problems, can be reduced to basic gates using one or two qubits. For spins, a one-qubit gate corresponds to rotation along two orthogonal directions and therefore relevant tests are observation of Rabi oscillations in pulsed ESR experiments, as previously discussed. Several experiments on mononuclear molecular spin centers have been performed as also reviewed in one article of this issue [23].

Next challenge is to perform conditioned quantum operations involving more than one spin center. In general terms, we need to demonstrate that the dynamics of one (*target*) spin is conditioned by the state of the second (*control*) spin [22]. This may require the two spins to be distinguishable either spatially or spectroscopically and a typical sequence for two-qubit gate encoding encompasses: the initialization of the system, the rotation of the *target* spin under different conditions of the *control* spin qubit and finally the read out of the system state. According to the specific pulse sequence and rotation, a number of two-qubit gates can be performed, similarly classical two-bit gates, such as controlled-NOT. This conditional spin dynamics is possible by exploiting quantum correlation (entanglement) of two of more spin centers and, since this is a genuine quantum property, quantum gates essentially different from classical gates.

Spin correlation (entanglement) is intrinsic property of system states that needs to be properly quantified by using suitable experimental quantities or mathematical functions [24]. Spin entanglement can be obtained within a single molecule or at supramolecular level (i.e. between molecules) by controlling spin topology and magnetic interactions. Along this line, dimers of molecular spins with weak permanent magnetic coupling could be designed and synthesized [25] and sizable spin entanglement was demonstrated [26]. One issue of this approach is related to the fact that, during the gate operation, the coupling between the two qubits needs to be switched on

and off in order to allow independent rotation of the two spin qubits. In other words, switchable links would be required. This problem can be solved by engineering the molecular states in such a way to make use of auxiliary states [27] as also described in the realistic case of antiferromagnetic rings [28]. An alternative way to entangle two spins is to simply position two spin centers at fixed distance (few *nm)* and exploit dipolar (i.e. *through space)* interaction as done for spin defects in diamond [29] and Si. The drawback of using dipolar interaction is, however, its persistent character and its strong dependence on both distance and orientation of the two spin centers. These make such an approach not simply scalable for defects. Maybe this problem is less critical for molecular assemblies. A further alternative way to entangle two spin centers far apart is, however, the use of flying qubits (photons) as demonstrated in a recent experiment in which entanglement between two NV centers distant 25nm from one another was achieved by engineering the pulse sequence and using dynamic decoupling technique [30].

Proposals for the implementation of two-qubit gates with specific molecular spins systems have appeared and preliminary experiments have been reported using binuclear lanthanides [31], radicals [32], antiferromagnetic rings [33]. Moreover, an intense search of suitable bi-nuclear molecular system is currently under way and many potential candidates are ready to be tested. In terms of experiments, this would require the use of multi-frequency spectrometers that allow to distinguish the two qubits or to activate switchable interaction. Commercial instrumentation, such as that for Pulsed Electron-Electron Double Resonance (PELDOR), is well developed but, in most of the cases, it needs be adapted to working conditions (frequency, temperature, magnetic field) of molecular qubit. At present, dedicated instrumentation is accessible only to few laboratories worldwide whist the implementation of two-qubit gates with molecular spin ensembles would require more flexibility/tunability on both molecular qubits and instrumentation. Moreover, in spite of the progress achieved in using pulse ESR techniques to molecular electron spins [34], much work still remains to be done to encompass inhomogeneities of both molecular features and applied field and, more in general, to efficiently decouple spin to the environment. For instance, very interesting results have been obtained in the optimization of pulse sequences for dynamical decoupling [35]. In view of using multi-frequency pulse spectrometer, it is worth to remind that magnetic molecules generally possess both electron and nuclear spins and probably the best approach will be to combine the long coherence time of nuclear spins with the faster manipulation and read out of electronic spins. For this ENDOR technique offers several interesting solutions as discussed in ref.36.

Final general remark should be done concerning the use of spin ensembles. The main criticism, well known in the QC community for NMR, is that working with ensembles makes the systems not –easily- scalable**.** In other words, the resources, (eg spins) required for solving problems and for the relative error correction, scale fast with increasing number of data, thus making this type of architectures not suitable for a universal use. Within a more pragmatic perspective, we may focus our interest on quantum simulators [37], i.e. small quantum computers that solve only specific problems which would require huge amount of classical computing resources, or even intractable by classical computers. In practice this requires the use of molecular derivatives comprising small but well defined spin clusters whose dynamics may solve a complex problem or emulate the behavior of system of interest in other fields (for instance a chemical reaction or a problem in solid state physics, see also review article in this issue [38]). This topic is still largely unexplored and deserves joint effort from chemists and physicists.

3. Molecular Quantum Spintronics

The addressing, manipulation and read out of **single molecular objects** constitute the next big conceptual and technological challenge. If we can avoid some of the drawbacks found in using spin ensembles, here we have to find efficient ways to detect tiny magnetic signals and to individually manipulate spins by protecting fragile quantum states from the environment at the same time.

Different approaches have been tested to detect tiny magnetic signals: one milestone was the development of **nano-SQUID** made with carbon nanotube [39]. Despite the magnetic flux sensitivity of these devices can achieve the quantum limit, the main limitation of this type of magnetometers is constituted by the magnetic coupling - through space- of the molecule with the sensor. Direct single molecule detection by charge current seems more appealing, at least for spintronic devices, and it may benefit from the progresses achieved in close fields such as molecular electronics, scanning microscopy and single-electron semiconducting devices.

The use of **scanning probes**, more specifically tunneling tips, holds much promise for their potentialities to localize, move and read out single magnetic atoms and molecules [40]. With respect to bare magnetic atoms, the presence of an organic ligand seems to delocalize the magnetic features of the molecule [41] and data interpretation is still under debate. Recently interesting experiments on the manipulation and read out of molecular spin ($TbPc_2$) by radio frequency [42] and single magnetic atom on a surface by pulse-MW sequences have been reported [43].

At the same time, the development of **tunnel junctions** that may host a single molecule (fig.2) have been independently reported by different groups. Magnetic features of individual molecules have been observed and reported for Fe_4 [44, 45], $TbPc_2$ [46] organic radicals [47]. An open question here is how the charge current from the leads perturbs the magnetic state of the molecule. Changes of valence (and spin) state of the magnetic core are indeed expected. Since each type of molecule behaves in different way, this issue needs to be evaluated case by case. An alternative read out scheme comprises a quantum dot whose conductivity is affected by the spin state of the magnetic center that is in close proximity and coupled with the device. This scheme is analogous to the spin dependent tunneling that is used to read out spin qubits also in semiconductors, but here the **quantum dot** can be made by CNT [48], graphene nano-constrictions [49] or even the organic radical present in the ligand of the molecule as demonstrated in the case of $TbPc_2$ molecular spin transistor [50]. In this scheme, the charge channel and the spin center are two separate bodies, coupled by exchange interaction (see fig.3).

The experiments reported by the Grenoble team went a step ahead demonstrating the possibility to read out and manipulate the nuclear spin state. The nuclear spin of Tb (I=3/2) is indeed coupled to the electron magnetic moment (ground state J=6, $m_J=\pm 6$) by the hyperfine interaction (fig.3) giving rise to hybrid electron-nuclear states whose level anticrossing (LAC) are well visible at low magnetic field. The nuclear states can be identified by sweeping magnetic field and comparing the position of the LACs with those measured on bulk samples. Note that, since measurements are performed on a single qubit, the process must be repeated several times in order to get a significant statistics.

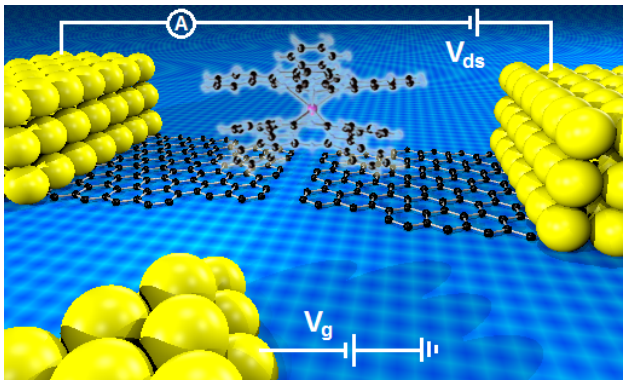

Figure 2: Molecular spin transistor made by graphene electrodes and $TbPc_2$ molecule. In this case graphene based electrodes are used to contact $TbPc_2$ molecule. (Reproduced from Ref. 51 with permission from the Consiglio Nazionale delle Ricerche (CNR) and The Royal Society of Chemistry.)

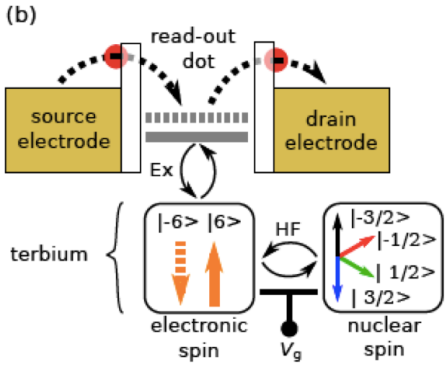

Figure 3 Scheme of functioning for molecular spin transistor with separate quantum dot (Pc radical) in which charge can tunnel from electrodes, the electron magnetic moment J=6 and nuclear spin (I=3/2) of Tb^{3+} ion (Reproduced from Ref. 54 with permission from The American Association for the Advancement of Science)

By exploiting the long coherence time of nuclear spin (coherence time exceeding 60μs) and the hyperfine electric Stark effect, the same team has then demonstrated that it is possible to manipulate the nuclear spin of a single molecule. More specifically nuclear spin trajectories [52] and Ramsey fringes have been observed [53]. These results compare well with similar experiments reported for spin impurity (P donor) in Si [54] and witness a tangible contribution of molecular magnetism to QT. At the same time, we expect that the next steps along this research line will move in parallel with similar devices based on spin impurities in semiconductors [55] or NV centers in diamond [56], that is, the implementation of two-qubit gates or multi-qubit algorithms.

Different schemes can be envisaged for the implementation of two-qubit gate with molecular spintronic devices: a CNT may host two (or more) molecules and several gate electrodes that can act to switch on and off interaction between molecules. Alternatively, a suitable bi-nuclear molecule within a junction can be used as molecular hardware. In both cases, spin manipulation can be done by addressing each spin center by microwaves using suitable pulse sequences.

Working devices need to be reliable and suitable **quantum error correction protocols** are to be developed. The problem of error correction is well known in computer science and some schemes are discussed in textbooks [22]. Briefly, it may occur that during a quantum operation a qubit accidently flips, invalidating the whole process. To mitigate and correct these errors we may encode the qubit in more than one (typically 3) processor and then use the majority rule: if the probability of accidental flip is relatively low, 2 qubits over 3 remain in the correct state while one contains error. In this case the majority (2 over 3) determine the correct state while the third one can be corrected. Further methods to correct different type of quantum errors have been reported in the literature for other spin systems, in particular those tested for NV centers [57].

The previous discussion leads us to another technological issue: soon or later we'd need to have arrays of similar devices working at the same time in order to guarantee the scalability of our computing machine. Although this aspect is less discussed in literature, the rate of success R in the device fabrication process is relatively low (often <10%). These numbers are typical for tunnel junctions in molecular electronics although they related to the specific fabrication process and certainly need -and can- be improved in future by exploiting novel bottom-up fabrication methods. It should be noted, however, that also the fabrication of CMOS-compatible quantum devices below 10nm by top-down (lithographic) techniques are affected by low yields. In view of applications, it is worth to fix some benchmarks that may assess the reliability of the fabrication process. As an example, let us suppose we intend to test a quantum error correction protocol. As mentioned above, we'd need at least three identical devices and in this case the probability to get all these working at the same time will drop at R^3. Thus, we would need to fabricate 10^3 devices to get at least 1 working machine to test quantum error correction code!

Concerning multi-qubit devices, recently the implementation of **Grover's algorithms** within the ground state multiplet of a single molecule [58] has been carried out at the L. Néel institute

laboratory [59]. The Grover's algorithm efficiently solves a specific problem by performing a search of an item within a set of data. The sub-levels of the ground multiplet inequivalently spaced in energy, such as the mixed nuclear-electronic states of $TbPc_2$, constitute an excellent playground to test this scheme since each of them can be addressed separately by microwave pulses. Note that in this scheme, spin entanglement is not required, so the scheme can be implemented within a single molecule. As a proof of concept, few sub-levels can be considered but it is worth to mention that the implementation is hardly scalable by using a single molecule. It is nevertheless worth to highlight here that, so far, the Grover's algorithm has been implemented with trapped ions, photons and superconducting qubits but, for the best of our knowledge, not with other solid state platform such as impurity in Si: this, once more, testifies the pioneering role of molecular spin in the field of Quantum Technologies.

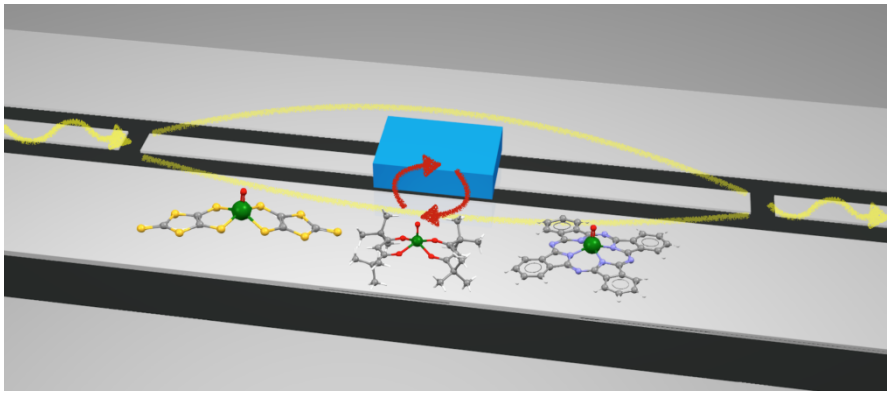

Figure 4. Artistic view of molecular spin coupled to planar superconducting resonators.

4. Molecular spins in hybrid quantum architectures.

The ability to manipulate and read out an arbitrary spin state in a molecule is certainly pre-requisite to be good candidates for quantum information processing. Yet, other features are required in view of wider exploitation of molecular spins for quantum technologies. One of this is the possibility to exchange quantum information between solid state registers (spins) and flying qubits (photons). Molecules offer a broad spectrum of frequencies for an efficient coupling with photons: nuclear spins are active at radio frequencies (MHz) while the pattern of magnetic energy levels of electron spins fully covers the microwave (MW) range (GHz). Several molecules are also active in the visible range and, interestingly, their response can be sensitive to their spin state. Again, the main challenge is to *coherently* couple the spin with photons, that is the match in energy should occur along with the transfer of phase information. This implies that the spin manipulation should be fast enough to overcome the decoherence mechanisms of both the spin and photon systems. Key experiments in this context make use of microwave resonant cavities with high quality factor in which long-lived photons trapped in the cavity couple with spins (fig.4). First tests are typically performed in continuous wave operation mode, although the final goal is to get hybrid devices in which quantum information are exchanged through MW pulse sequences. Coherent spin-photon states are obtained in the so-called *strong coupling regime* for which the spin-photon coupling is stronger than each decoherence rate of spins and photons [7]. Again, only molecular spins with the longest coherence time are suitable to pass this test. Spin can couple with the magnetic component of radiation B_1 through their dipole $g\mu_n S$, yet this interaction is in general very weak and we need to develop strategies to enhance it. Molecular engineering may allow to enhance both the Landé g-factor and the total magnetic moment of the ground multiplet beyond ordinary values obtained for single atoms. Another strategy to strengthen the spin-photon coupling is to use spin ensembles. It has been demonstrated in fact that the spin-photon coupling can be enhanced by a factor $\sqrt{N}$ – with N total number of spins- by using collective modes [7]. Although the general problem of coupling photons with two-level system (eg. atoms, molecules with *electric* dipoles etc.)

315 is well documented in literature, only recently experimental investigations focused on spin systems.
316 Strong coupling regime was achieved by using conventional superconducting resonators and NV
317 centers [60] or Er spin impurities in inorganic matrix [61] at mK temperature. We are currently
318 using high T_c superconducting planar resonators [62] that show excellent performances at finite
319 temperature (up to 50K, at least) and in strong magnetic field and, with these, we can achieve
320 strong coupling regime with DPPH [60] and PyBTM [63] organic radicals at liquid helium
321 temperature and even above. It is worth to note that in this latter cases the strong coupling regime
322 was obtained by using concentrate samples that present sharp EPR lines due to exchange
323 narrowing. As concerns mononuclear molecular metal-spin centers, preliminary results on diluted
324 crystals show that we get close -but not yet fully in- to the strong coupling regime [64]. For
325 comparison, a snapshot summary of these preliminary results is plotted in fig.5. It should be
326 emphasized, however, that data reported in fig.5 depend only in part on the intrinsic features of the
327 spin centers. Other parameters, such as temperature, number of spins, cavity characteristics,
328 influence both the spin-photon coupling and the spin resonance linewidth. Thus, for instance, in
329 fig.4 different values are reported for same derivative at different temperatures or spin
330 concentrations. Results on $Cu(nmt)_2$ crystals are quite encouraging: if we extrapolate trend at low
331 temperature (open symbols) we can safely expect that the strong coupling regime can be achieved
332 below 1K.
333 An alternative approach is to locally enhance the intensity of MW radiation. It has been
334 proposed indeed that nano-structured superconducting strip lines may allow to achieve strong
335 coupling regime even with a single (molecular) spin and this can be used for scalable architectures
336 [65]. Experiments are currently testing different solutions since the detection of tiny signals requires
337 extraordinary sensitivity. By using Josephson Junctions amplification, the detection of small
338 ensemble of about 10^3 spins has been reported and this is, at present, the best performance of EPR
339 nano-detection [66]. The use of electric field component to manipulate spins is a further attractive
340 alternative and several mechanisms have been proposed [67] and they are currently under
341 investigation [68].
342 Achieving strong coupling regime with microwave photons allow to integrate molecular spins
343 in hybrid quantum devices. Superconducting circuits are normally used as a bus to transfer
344 quantum information between different quantum memories and registers. In a recent experiment,
345 we have demonstrated that we can couple two or more distinguished spin ensembles through
346 resonant microwaves photons by spectroscopic measurements [63]. Next steps along this line could
347 be the integration of molecular spins in more complex superconducting circuits with the encoding
348 of sequences of MW pulses. This will eventually allow to perform quantum algorithms [69] or
349 simply to transfer qubit from fast quantum registers to memories. Along this line, pulse MW
350 sequences have been used to efficiently transfer qubits in hybrid superconducting circuits with NV
351 centers [70]. Again, we may learn a lot from fields close to molecular magnetism!
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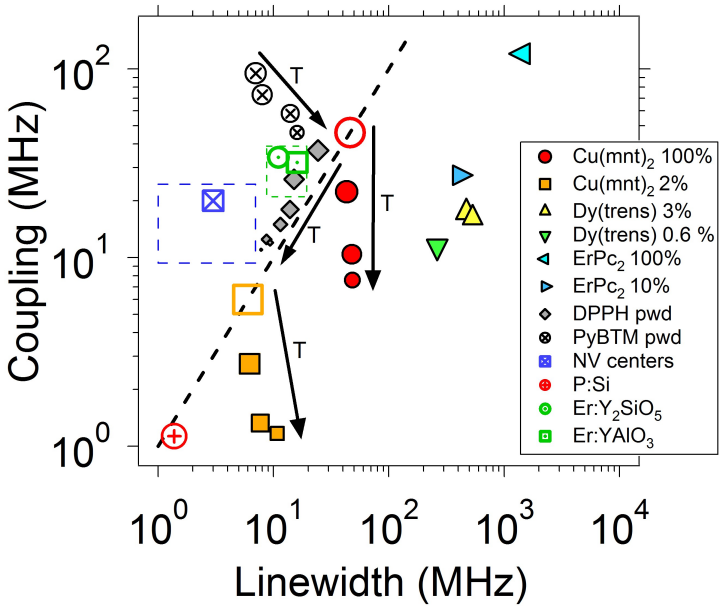

Figure 5 Coupling strength against spin linewidth parameters as measured in different molecular spins systems. Results can be compared with those obtained with NV centers and Er spin defects in YSio or YAlO. The parameters of DPPH and PyBTM organic radicals are taken from ref. 62 and 63 respectively. Data taken at different temperatures are indicated by the black arrows and by symbols of different sizes that range from 2 K (larger symbols) to 50 K (smaller symbols). Empty symbols display the parameters extrapolated to 0.3 K. The dashed line represent the threshold above which strong coupling is achieved. Dashed rectangles show the typical working ranges used for NV centers (blue) and Er spin centers (green) coupled to superconducting Nb planar resonators at mK temperature region. (Reproduced from Ref. 64 with permission from the Consiglio Nazionale delle Ricerche (CNR) and The Royal Society of Chemistry.)

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