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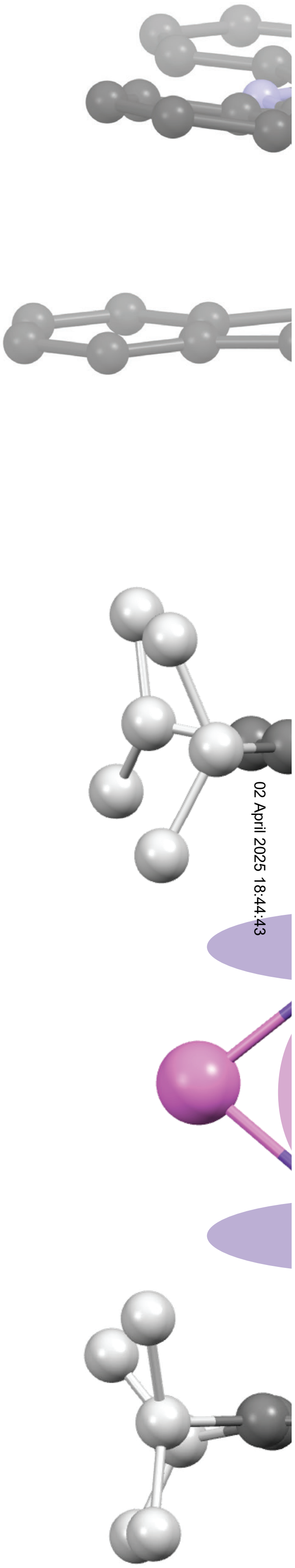

MAKING QUBITS FROM MAGNETIC MOLECULES

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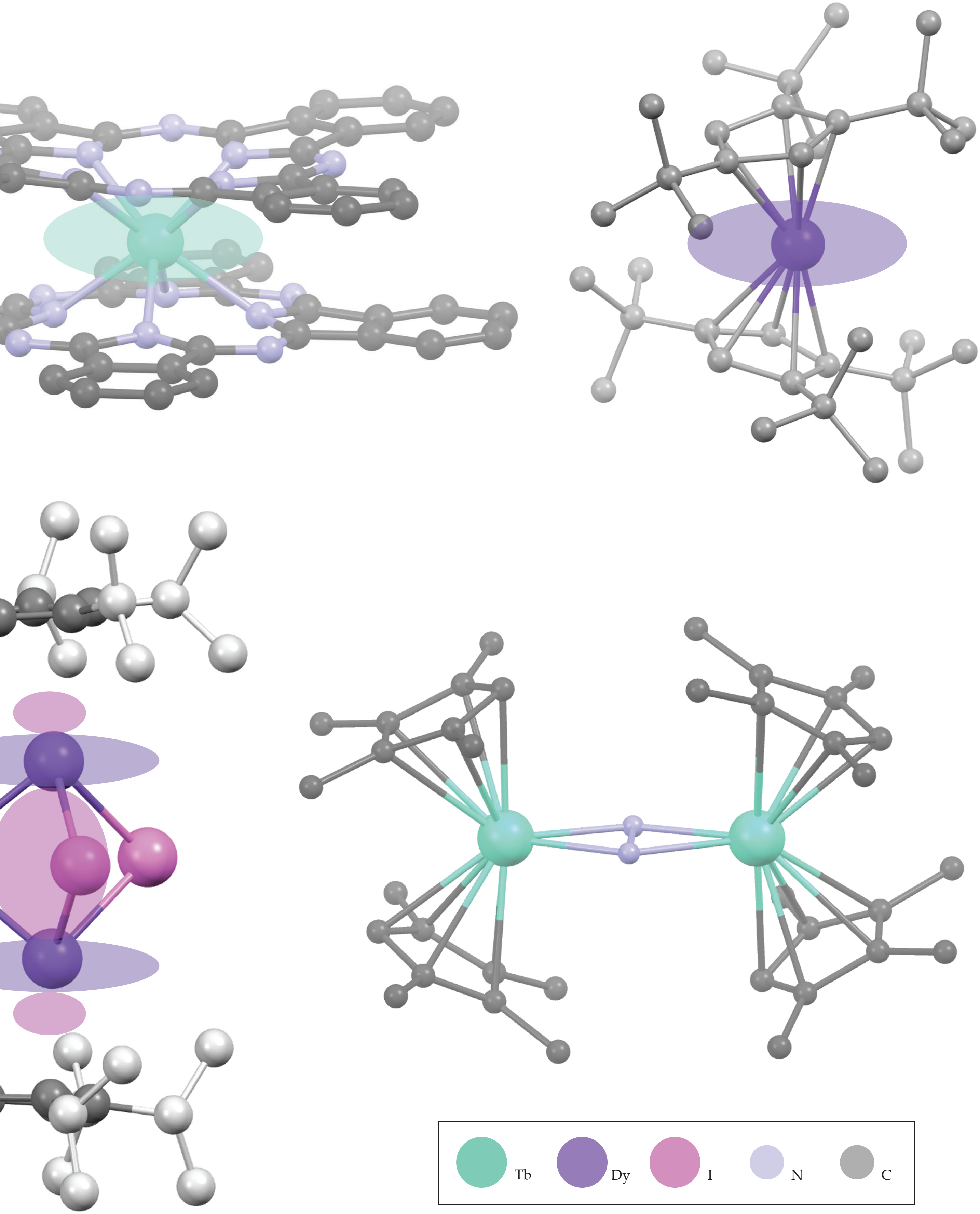

The evolution of magnetic molecules. Lanthanide-based [Tb(Pc)$_2$]$^-$ (top left) and [Dy(Cp$^{\mathrm{ttt}}$)$_2$]$^+$ (top right) have oblate 4*f* densities (exaggerated here) that enhance magnetic anisotropy. Two lanthanide atoms can increase the magnetic moment; examples include [(Cp$_2^{\mathrm{Me4H}}$Tb)$_2$N$_2$]$^-$ (bottom right) and (Cp$^{\mathrm{iPr5}}$)$_2$Dy$_2$I$_3$ (bottom left), which has shared dysprosium 5d_{z^2} orbitals. (Pc^{2-} is a phthalocyanine dianion, and Cp$^-$, a cyclopentadienyl anion; superscripts refer to organic substitutions on Cp$^-$ rings.)

The idea that a molecule could act as a magnet that manifests previously unobserved quantum behavior can be traced to theoretical predictions of a magnetic analogue to quantum mechanical tunneling of a particle through a potential energy barrier. The magnetic version would involve tunneling through an energy barrier that hinders reorientation of the magnet's north and south poles. Observation of the effect would require measurements on nanoscale objects that are much smaller than any that could be fabricated via the top-down methods—involving shrinking larger objects—that were available at the time that the idea first emerged.

An important breakthrough came from studies of molecular metal oxide clusters created via bottom-up, atom-by-atom chemical synthesis. The molecules were designed to mimic protein reaction centers, which play important roles in various biological processes, including photosynthesis. They would lead to the first demonstration of magnetic bistability—in which a magnetic dipole can be switched between the up and down metastable states—of purely molecular origin[1] and give rise to the term "single-molecule magnet." An SMM is an isolated molecule that can be magnetized and retain alignment of its north and south poles below a characteristic temperature, known as the blocking temperature.

Magnetic bistability can be observed through hysteresis, in which magnetic behavior is history dependent. The underlying physics of magnetic bistability in tiny particles was established by research on nanoparticles that were fabricated via traditional top-down methods for their potential use in classical information storage. As shown by the gray line in figure 1a, the particles will retain a preferred magnetic alignment, or polarity, while being subjected to a changing magnetic field, until the applied field is strong enough to reverse the polarity.

The first SMM ever made contained 12 magnetic manganese ions (see figure 1a), coupled by weak interactions through bridging oxygen atoms; that coupling produces a ground state with a collective magnetic moment of 20 μ_B (1 μ_B is the magnitude of a lone electron's magnetic moment). The energy barrier to reorientation of that moment is rather low, about 6 meV, and results in a blocking temperature of just 4 K. Above that temperature, thermal excitations cause the alignment of the magnetic moment to fluctuate (see figure 1b).

Quantum tunneling of magnetization

A significant discovery arose from studies of Mn_{12} crystals: periodic steps in magnetic hysteresis curves[2] (see figure 1a). The behavior is attributed to the previously predicted quantum tunneling of magnetization (QTM). Analogous to the quantized energy levels of a particle in a box, the allowed magnetic-moment orientations and the corresponding energies of an SMM are quantized (see figure 1b). Because Mn_{12} has 20 unpaired electrons, there are multiple quantum states (discrete orientations) on each side of the barrier, as opposed to just the up and down states for a single electron.

A magnetic field applied along the preferred magnetization axis—the so-called easy axis—tilts the energy landscape to favor states with aligned (up) magnetic moments (see figure 1b). When the field is swept, magnetic levels on opposite sides of the energy barrier are brought into and out of resonance. When on resonance, the magnetization has a finite probability of tunneling through the barrier. Through QTM, SMMs with magnetic moments pointing down may reorient, or relax, toward the up state; in contrast, classical relaxation over the energy barrier requires the help of thermal energy. As a manifestation of QTM, steps in the macroscopic magnetization of the crystal thus reveal the quantum nature of the Mn_{12} SMMs.

The discovery of resonant QTM opened up a new playground for physicists to explore quantum magnetization dynamics. Meanwhile, chemists realized that they could exert remarkable synthetic control over the magnetic interactions responsible for QTM and the magnetic energy barrier. The result was an interdisciplinary field that continues to grow.

Much effort has been directed toward increasing SMM blocking temperatures, with the lofty goal of designing SMMs that function as classical memory storage at liquid-nitrogen temperatures (77 K) and above. That would enable data storage densities of 100 Tb/in^2 (16 Tb/cm^2), two orders of magnitude higher than modern commercial devices. But therein lies a fundamental tension: QTM accelerates magnetization relaxation and is, therefore, detrimental to classical information storage. Physicists, however, recognized that magnetic molecules could potentially lead to next-generation quantum technologies.

Indeed, early theoretical work demonstrated the possibility of performing a quantum search algorithm using the discrete states of the Mn_{12} molecule.[3] That led to a bifurcation of effort: Work continued on improving SMM properties for classical data storage, while a new thrust emerged on developing molecular spin qubits.

Improving SMMs for classical data storage would require shutting down QTM and creating molecules with signifi-

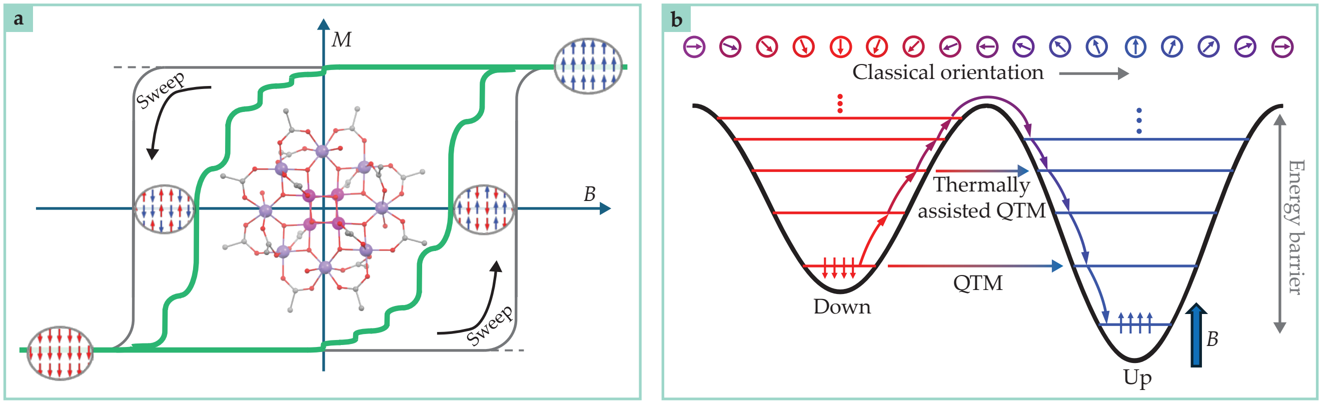

FIGURE 1. (a) THE CLASSICAL MAGNETIZATION RESPONSE (gray lines) of nanomagnets subjected to an applied magnetic field *B* contrasts with the stepwise response (green lines) of single-molecule magnets (SMMs), such as manganese-12 acetate, shown at center[1] (Mn^{4+}, pink; Mn^{3+}, purple; oxygen, red; carbon, gray). At low temperatures, the magnetization *M* saturates when the applied field is strong enough to overcome the energy barrier to spin reorientation (red and blue arrows). Stepwise relaxation is produced by quantum tunneling of magnetization (QTM).[2] **(b)** The classical dependence of energy on magnetic orientation is shown by the black curve; horizontal lines denote quantized SMM energy levels. An applied magnetic field tilts the energy landscape to favor up-oriented magnetic moments. Classical magnetization reversal occurs via thermal activation over the barrier. Relaxation through the barrier can occur by QTM with or without the input of thermal energy.

cantly greater energy barriers. Molecular symmetry, which chemists can control, plays a crucial role: In a cylindrically symmetric system, the magnetic quantum states are orthogonal, so QTM does not occur. Although no molecule has perfect cylindrical symmetry, maintaining a high symmetry helps. (Mn_{12} has a fourfold axial symmetry, as seen in figure 1a). Increasing the collective magnetic moment of an SMM also suppresses QTM, in the same way that increasing particle size diminishes the probability of spatial tunneling.

A molecule's magnetic moment arises from both the orbital and spin momenta of unpaired electrons. It is the orbital momentum that responds to the local molecular structure and produces the interactions that pin the magnetic moment along a preferred axis. Transition metals' *d* orbital electrons tend to participate in chemical bonding, which dramatically suppresses the orbital momentum and results in low SMM energy barriers. That fundamental limitation brought work with transition metals to a stall.

Transition to lanthanides

A major advance was made when a single terbium ion encapsulated between two dianions of the organic molecule phthalocyanine (Pc^{2-}; shown in the top left of the opening image) was found to display SMM behavior with a classical energy barrier of about 75 meV, more than an order-of-magnitude increase relative to Mn_{12}.[4] The magnetism of Tb^{3+} and other lanthanide (Ln) ions arises from unpaired electrons in contracted 4*f* orbitals. Unlike *d* orbital electrons, those unpaired electrons do not participate directly in chemical bonding, and thus they enhance the orbital contribution to magnetism relative to transition metals.

For Ln compounds, the energy barrier arises from the electrostatic interaction between the anisotropic 4*f* electron density and the electric field imposed by the host ligands—the nonmagnetic, often organic portion of the molecule that bonds to the magnetic ion. Emerging design strategies, primarily involving dysprosium and Tb,[5] have produced a huge number of new SMMs with barriers exceeding Mn_{12} by more than an order of magnitude.

Tb^{3+} and Dy^{3+} make the best SMMs because they have large spin–orbital magnetic moments and the most pronounced anisotropies of their 4*f* electron densities. Dy^{3+} also benefits from a fundamental theorem in quantum mechanics for systems with an odd number of unpaired electrons (Dy^{3+} has five); the theorem strictly forbids QTM in the absence of a magnetic field. Despite the much larger classical energy barriers in Ln-based SMMs, however, increases in blocking temperature were initially modest. The main reason is the onset of additional through-barrier relaxation via thermally assisted mechanisms involving QTM (see figure 1b) and short-lived virtual quantum states produced by vibrationally assisted Raman processes.

Researchers recognized that the optimum SMMs, designed for pseudo-cylindrical symmetry, would involve Dy^{3+} with axial ligands but no equatorial ligands, which would disrupt symmetry and promote QTM. It required some remarkable chemistry to realize such a molecule ($Dy(Cp)_2$; see the opening image, top right), which includes a pair of

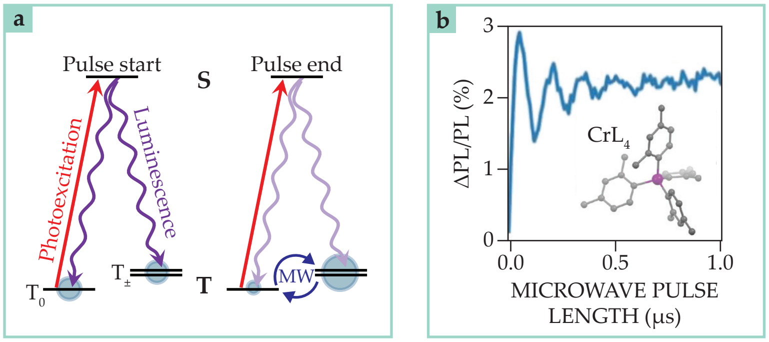

FIGURE 2. SPIN-DEPENDENT OPTICAL ACTIVITY means that a microwave-controlled qubit state is observable via photoluminescence (PL). **(a)** Excitation from the ground triplet level T_0 to the excited singlet state S and accompanying luminescence back to the T_0, T_+, or T_- triplet level drives the spin population (blue circles) from T_0 into the $T_\pm$ states, which alters PL intensity. Manipulation of the spin population between triplet states using pulsed microwave (MW) radiation can thus be monitored via changes in PL intensity. **(b)** Coherent microwave cycling, known as Rabi oscillation, of the spin population between triplet levels is measured by changes in PL emissions; the inset depicts the CrL_4 molecule, with parts of the ligand (L) that are amenable to chemical tuning highlighted. (Images adapted from ref. 12.)

cyclopentadienyl (Cp^-) ligands[6] and has a sandwich structure similar to $Tb(Pc)_2$ (see the opening image, top left). There are some key differences, however: Compared with Pc^{2-}, Cp^- is more compact, which produces a much stronger interaction with the oblate Dy^{3+} 4*f* electron density and leads to a huge classical energy barrier of about 250 meV.

Bulky substituents—affectionately termed "shrubbery"—on Cp^- rings prevent equatorial interactions with the Dy that promote QTM. Cp^- rings are also extremely rigid, which leads to high-frequency intramolecular vibrations. Additionally, the shrubbery lowers intermolecular phonon frequencies so that vibrations are sparse in the intermediate frequency range required to promote under-barrier Raman relaxation. The resulting $Dy(Cp)_2$ SMM maximizes performance based on the magnitude of the barrier, with blocking temperatures that approach 77 K.[6]

Fundamental limits

Despite remarkable progress, SMMs based on single Ln^{3+} ions have hit fundamental limits. Their magnetic moments are dictated by atomic, not molecular, considerations. And molecular chemistry does not allow further concentration of negative axial charge close to Ln^{3+} ions. Work on other oxidation states (Ln^{2+} and Ln^{4+}) is challenging and runs into the same issues. Hence, there is little scope for improvement. The only solution, therefore, is to couple multiple Ln ions. That, however, represents a monumental task. Standard synthetic strategies tend to result in weak coupling between Ln magnetic moments because of the contracted nature of 4*f* orbitals, particularly for Ln^{3+}. The moments therefore tend to relax independently in molecules containing multiple Ln^{3+} ions.

One solution to weak coupling involves bridging the ions with ligands that are radicals—that is, they themselves possess an unpaired electron. Direct overlap of the Ln 4*f* density with the diffuse spin density on the ligand leads to enhanced magnetic interactions. By bridging two Tb^{3+} ions with a N_2^{3-} radical (see the opening image, bottom right), Jeffrey Long, William Evans, and coworkers achieved an SMM with a large spin–orbital moment and a blocking temperature of 14 K,[7] which held the record until the discovery of $Dy(Cp)_2$.

Coupling via the extra, odd radical electron also shuts down QTM, leading to greatly enhanced magnetic coercivity (the field needed to flip the magnetization of the SMM). One may rationalize that effect on the basis that simultaneous QTM of two Ln moments is far less probable than one. The Ln moments, however, may start to relax independently once the thermal energy exceeds the coupling interaction energy. Moreover, the side-by-side arrangement reduces the overall axiality at each Ln site in the SMM (shown in the opening image, bottom right). Those factors contribute to relatively low blocking temperatures. Consequently, a set of even-more-demanding design challenges emerges: further enhancing Ln–Ln coupling while also maintaining axiality.

The strongest magnetic coupling (up to an electron volt) arises between electrons that reside on the same atom or occupy the same set of molecular orbitals. The question, then, is whether direct magnetic orbital overlap within a Ln_2 molecule can be achieved. The contracted nature of the 4*f* shell makes that almost impossible for Ln^{3+}. In some cases, however, an electron added to a Ln^{3+} ion (reducing the oxidation state to Ln^{2+}) will occupy a more extended 5*d* orbital rather than the open 4*f* shell. The 5*d* orbital offers a possible strategy for achieving direct orbital overlap. Long and coworkers have employed that approach by sandwiching a pair of Dy ions between two rigid Cp^- ligands, with three iodide (I^-) ligands holding everything together[8] (see the opening image, bottom left).

In the $(Cp)_2Dy_2I_3$ molecule, an extra electron is shared between the Dy^{3+} ions. It occupies overlapping, hybridized 5*d* orbitals, thus mediating strong magnetic coupling. The result is a highly robust and large spin–orbital magnetic moment. Moreover, the molecular geometry is highly axial, which gives rise to a classical energy barrier of about 300 meV. Blocking temperatures that approach 80 K emerge, with a coercivity exceeding 14 T at 60 K, surpassing even the coercivity of commercial samarium and neodymium magnets.

Molecular spin qubits

With the goal of classical storage in mind, the best examples of SMMs have been optimized to suppress QTM and behave classically. But quantum effects are appealing for a different type of memory application: the molecular spin qubit.

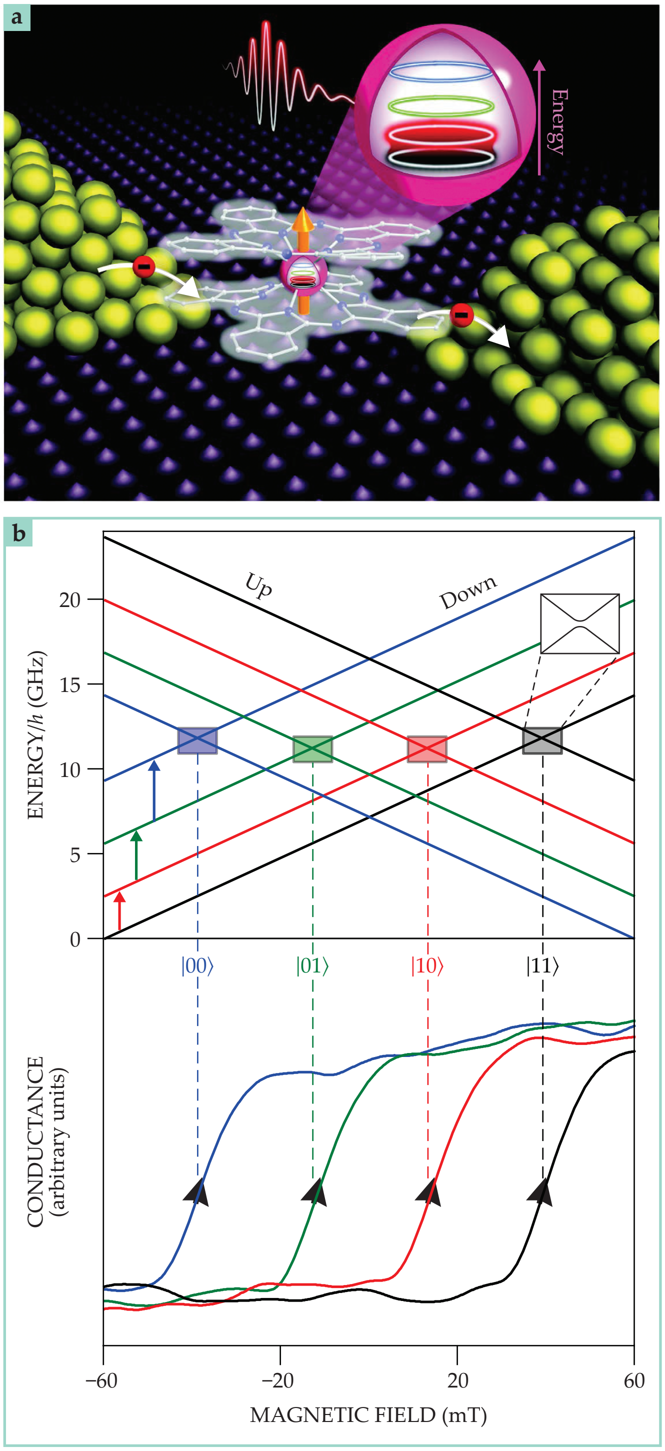

FIGURE 3. (a) A SINGLE-MOLECULE TRANSISTOR encodes information in the nuclear spin states of a single molecule. The single-molecule magnet Tb(Pc)$_2$ is anchored to gold source and drain electrodes. White arrows denote current flow; the orange arrow represents the electronic spin–orbital moment, and the inset depicts the four nuclear hyperfine levels encoding the qudit states |00⟩, |01⟩, |10⟩, and |11⟩. **(b)** In a magnetic field, the unequal splitting of the four nuclear hyperfine levels (here normalized by Planck's constant *h*) allows selective microwave mixing of nuclear states (colored arrows). Resonant quantum tunneling of magnetization (QTM) occurs when hyperfine levels associated with the same nuclear state meet (colored rectangles), whereupon they mix and undergo a so-called avoided crossing (inset). At ultralow temperatures (25 mK), that manifests as a jump in the transistor's conductance at specific values of the applied magnetic field, which enables electronic readout of the nuclear qudit. (Images adapted from ref. 13.)

The beauty of molecular chemistry is in its building-block approach. Start with a promising molecular spin system, make deliberate synthetic modifications to fine-tune the spin physics and coherence, build in additional functionality such as optical or electrical activity, and, finally, add linkers to facilitate intermolecular connectivity and attachment to suitable substrates. To a good approximation, each molecular spin qubit and the associated linkers are identical, which makes the approach scalable. In 2003, George Christou, colleagues, and I first demonstrated a method to link pairs of magnetic molecules and observe the quantum mechanical coupling between them,[9] akin to the coupling between spin qubits hosted in semiconductor quantum dots.

The simplest molecular spin qubit comprises a single unpaired electron: a quantum two-level system that is agile and can be coherently driven using microwave electromagnetic fields. In 2007, Arzhang Ardavan and coworkers considered the question of whether spin relaxation times in such a molecule, Cr$_7$Ni, would permit quantum information processing.[10] They concluded that energy relaxation (the decay between classical spin-up and spin-down states, also known as spin–lattice relaxation) is slow, and quantum memory times are limited by the coupling of spin qubits to the nuclear magnetic moments of surrounding hydrogens—that is, protons—of which there are typically many in molecular systems. Importantly, that work identified strategies for synthesizing molecules with improved quantum memory times, also known as coherence times.

The first wave of studies that followed focused on understanding and mitigating processes that contribute to electron spin relaxation in molecular qubits. The molecular approach enables exquisite chemical control in a way that is simply not possible in conventional solids. For example, by exploiting variations in the identity, rigidity, and coordination geometry of the ligands, chemists can exert direct control over the interactions that influence spin–lattice relaxation.[11] That control is important because spin–lattice relaxation ultimately limits quantum memory times, particularly at the elevated temperatures necessary for quantum sensing.

Low-temperature electron spin decoherence is mediated primarily by magnetic coupling to protons, which have large moments relative to other nuclei. That coupling results in unwanted entanglement with the environment. Nuclear isotope

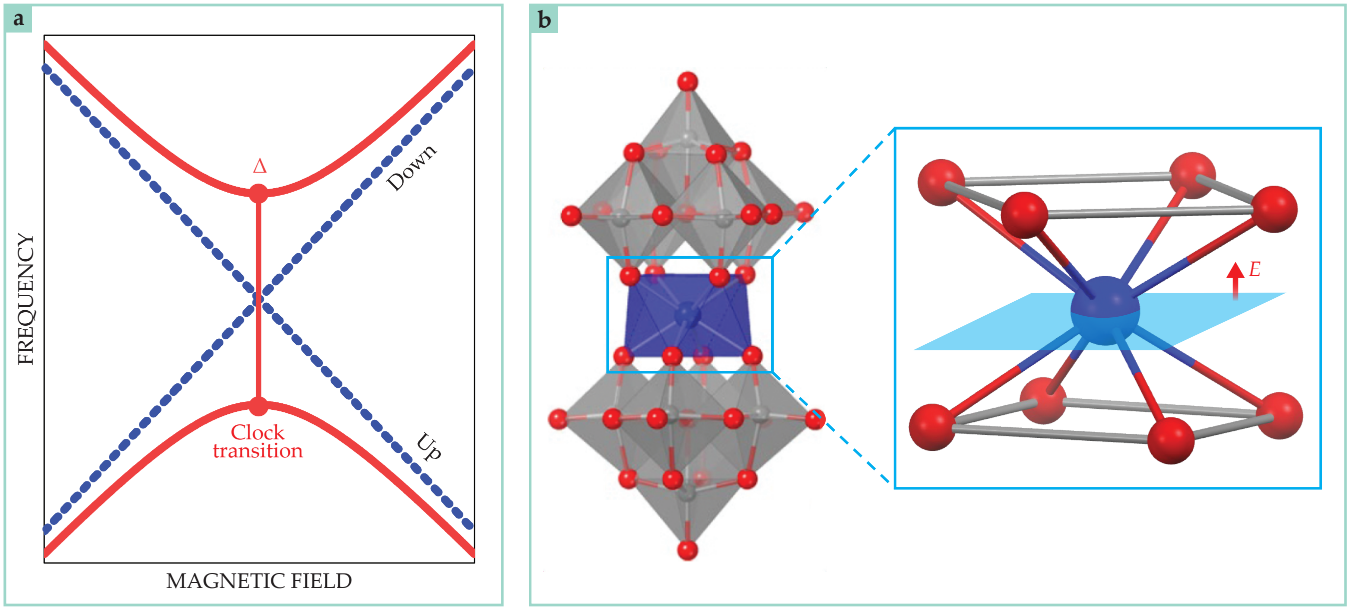

FIGURE 4. (a) CLOCK TRANSITIONS are avoided crossings between up and down magnetic states at certain values of the magnetic field. That physics is responsible for mixing single-molecule magnet (SMM) quantum states with opposing magnetizations; the gap minimum reflects the quantum tunneling of magnetization (QTM) frequency. The ideal SMM for classical memory storage has no gap (dashed lines). By contrast, spin qubits benefit from large QTM gap minima, where the transition frequency Δ is insensitive to magnetic field fluctuations, which leads to enhanced quantum memory coherence.[15] **(b)** The molecule $Ho(W_5O_{18})_2$ is shown here with an expanded view of its core. An applied electric field *E* displaces the Ho^{3+} ion from the midplane, thereby tuning the clock-transition frequency Δ. (Image adapted from ref. 16.)

labeling—for example, replacing ^1H with ^2H—allows for investigation of the physics and a means of controlling it. Also, by diluting molecular qubits in either solid or frozen solution matrices to suppress electron spin–spin relaxation, researchers have achieved quantum memory times approaching milliseconds at liquid-helium temperatures and microseconds at room temperature.[11]

Chemists and physicists are now working collaboratively on the next steps. Spin manipulation is usually achieved using magnetic resonance techniques, although they lack detection sensitivity and spatial resolution because of the millimeter microwave wavelengths employed at typical laboratory magnetic field strengths of 0–10 T. A major attraction of the nitrogen–vacancy (NV) defect center in diamond is its spin-dependent optical activity, which enables initialization and readout of individual qubits (see the article by Christopher Anderson and David Awschalom, Physics Today, August 2023, page 26). As demonstrated by Danna Freedman, David Awschalom, and colleagues, one can chemically engineer the same optical–spin interfaces in molecules.[12]

The Cr^{4+} ion has two electrons in partially filled *d* orbitals. A strong ligand then provides the necessary ingredients for optical spin-state initialization and readout. Those ingredients, sketched in figure 2, are a triplet ground state with aligned electron spins that can be coherently manipulated, using microwaves and narrow absorption lines in the near-IR, to an excited singlet state in which the spins are oppositely aligned. The combination of those two properties allows selective laser excitation from a targeted triplet level into the singlet state, followed by nonselective emission back to the triplet states.

The system can be initialized by optically pumping the spin population out of the given triplet level (see figure 2a). Microwave pulses can then be used to perform single-qubit operations between the triplet levels (see figure 2b), with a final readout of the spin population achieved by monitoring changes in the photoluminescence emission. Crucially, chemists can fine-tune the optical–spin interface to move the field forward.[12]

A single-molecule transistor

One of the landmark results in molecular magnetism is the implementation of a quantum search algorithm that uses the nuclear spin states associated with a $Tb(Pc)_2$ SMM trapped in a single-molecule transistor[13] (see figure 3a). The method relies on the bistability of the Tb^{3+} ion's spin–orbital moment, which can flip via resonant QTM only when there are avoided crossings, or gaps, between the lowest two electronic levels at specific magnetic field intensities (see figure 3b). Because of hyperfine coupling to the ^{159}Tb nucleus, those levels are further split into four nuclear sublevels. Consequently, the Tb^{3+} spin–orbital moment is sensitive to the quantum state of the nuclear qudit—a quantum system with *d* states, four in this case—and, when the spin–orbital moment flips, it induces a jump in the conductance of the transistor.

The magnetic field of the conductance jump therefore provides a direct readout of the molecule's nuclear state. It is then possible to perform quantum logic operations on the nuclear qudit states with selective microwave pulses and use the transistor for the final readout of the nuclear qudit state. Working in such a system, Wolfgang Wernsdorfer and coworkers generated a coherent superposition of the nuclear states and then used the transistor's localized microwave electric fields to evolve the system to the desired quantum state, thereby demonstrating, for the first time, the feasibility of molecular-scale quantum logic devices.[14]

Symmetry-lowering interactions in molecules such as $Tb(Pc)_2$ generate the avoided crossings between electronic levels; the size of the gap reflects the QTM frequency and is dictated by the degree of symmetry breaking. In 2016, some colleagues and I showed that a holmium molecule, $Ho(W_5O_{18})_2$, with pseudo-fourfold symmetry, hosts so-called clock transitions (see figure 4a), where the sensitivity of the qubit transition frequency to the variations in the local magnetic field vanishes.[15] (See Physics Today, May 2016, page 17.) That property results in decoupling of the qubit from most magnetic noise sources and leads to enhanced coherence and quantum memory times approaching 10 μs at 5 K.

Recent work has demonstrated electrical coupling to the spin in the $Ho(W_5O_{18})_2$ molecule.[16] An electric field applied along the pseudo-fourfold axis influences the displacement of the Ho^{3+} ion away from the midplane (see figure 4b), thereby affecting the ion's electric dipole moment. In turn, that displacement modulates the clock-transition frequency, again demonstrating the possibility of local electrical control of a spin qubit.

A drawback of $Ho(W_5O_{18})_2$ is fast spin–lattice relaxation, which ultimately limits the quantum memory time. That is because of the strong electronic coupling of the anisotropic 4*f* charge density to ligand vibrations. Several lutetium (Lu^{2+}) molecules have now been synthesized with a filled 4*f* shell and a lone unpaired electron occupying a mixed 5*d*/6*s* orbital. One of those molecules has a large clock-transition frequency of 9 GHz.[17] Crucially, the molecules have an almost-pure spin magnetic moment that is only weakly coupled to the surrounding ligand vibrations; that results in energy-relaxation times on the order of milliseconds, which leaves lots of room for further enhancement of quantum memory times.

Progress and future challenges

The past 10 years have witnessed significant breakthroughs in the field of molecular magnetism, with well over an order-of-magnitude increase in SMM blocking temperatures,[6,8] which were stagnant for the previous quarter century, and major advances in the performance of molecular spin qubits,[11] including development of optical[12] and electrical[13,16] interfaces. But much work remains to be done. In the case of SMMs, an important chemical step is scaling up the synthesis of molecules with three or more strongly coupled Ln moments. Molecules with metal–metal bonds between transition metals should also not be ruled out; the challenge in such systems will be to prevent quenching of the orbital moment that imparts the required magnetic anisotropy.

It will also be important to develop methods for addressing individual SMMs on nanometer length scales, which will require approaches for organizing molecules on surfaces or at interfaces.[18] That will be challenging because the current leading SMMs have an absence of equatorial ligands, which makes them highly reactive in all but the most inert environments.

In the area of quantum spin science, one can envision near-term sensing applications, perhaps in combination with targeted chemical sensitivity, something that is harder to achieve using existing solid-state spin qubits, such as NV centers. Realization of such applications will require further optimization of spin–lattice relaxation times for high-temperature operation. Although devices based on spin ensembles will surely have some utility, those applications should spur further chemical optimizations, with the ultimate goal of single-spin sensors.

In the longer term, wiring together molecular spin qubits is a critical step toward developing quantum logic gates. That will require chemical design of molecules with multiple quantum resources, such as electron–nuclear qudits and molecules with many coupled spin qubits. Further scale-up will require hybrid approaches that use optical or microwave photons or molecular wires, such as graphene ribbons,[18] to interconnect individual molecular spin qubits and for longer-range communications. Here, one can imagine selectively entangling pairs of molecular qubits by electrically bringing them into and out of resonance with a microwave transmission line. With continued rapid progress, there are real possibilities that molecules can contribute to next-generation quantum communication and computing.

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