Understanding the Spin of Metal Complexes from a Single-Molecule Perspective

Jie Guo, Qinghua Gao, Fei Gao,* Chuancheng Jia,* and Xuefeng Guo*

Compared with aggregate spin behavior, single-molecule spin behavior can be accurately understood, controlled, and applied at the level of basic building blocks. The potential of single-molecule electronic and nuclear spins for monitoring and control represents a beacon of promise for the advancement of molecular spin devices, which are fabricated by connecting a single molecule between two electrodes. Metal complexes, celebrated for their superior magnetic attributes, are widely used in the devices to explore spin effects. Moreover, single-molecule electrical techniques with high signal-to-noise ratio, temporal resolution, and reliability help to understand the spin characteristics. In this review, the focus is on the devices with metal complexes, especially single-molecule magnets, and systematically present experimental and theoretical state of the art of this field at the single-molecule level, including the fundamental concepts of the electronic and nuclear spin and their basic spin effects. Then, several experimental methods developed to regulate the spin characteristics of metal complexes at single-molecule level are introduced, as well as the corresponding intrinsic mechanisms. A brief discussion is provided on the comprehensive applications and the considerable challenges of single-molecule spin devices in detail, along with a prospect on the potential future directions of this field.

1. Introduction

Spin has special significance in physics and chemistry, where it provides an additional degree of freedom beyond charge. The spin degree of freedom offers a wide range of possibilities for electronic devices, showing extraordinary potential in transport, processing, and non-volatile memory.^[1–4] In general, spin comes from two parts, namely electron spin and nuclear spin. Among them, electron spin has been extensively studied,^[5] and the comprehensive utilization of electronics with spin degrees of

J. Guo, Q. Gao, F. Gao, C. Jia, X. Guo
Center of Single-Molecule Sciences
Institute of Modern Optics
Frontiers Science Center for New Organic Matter
Tianjin Key Laboratory of Micro-Scale Optical Information Science and
Technology
College of Electronic Information and Optical Engineering
Nankai University
38 Tongyan Road, Jinnan District, Tianjin 300350, P. R. China
E-mail: fei.gao@dipc.org; jiacc@nankai.edu.cn; guoxf@pku.edu.cn
The ORCID identification number(s) for the author(s) of this article

can be found under https://doi.org/10.1002/smtd.202401302

F. Gao Donostia International Physics Center

Manuel Lardizabal Ibilbidea 4, Donostia-San Sebastián 20018, Spain X. Guo

Beijing National Laboratory for Molecular Sciences National Biomedical Imaging Center College of Chemistry and Molecular Engineering Peking University Beijing 100871, P. R. China

freedom has become a promising field, called spintronics.^[6] Spintronic systems take advantage of the fact that the electron current consists of spin-up and down carriers.^[7] On the other hand, nuclear spin, an important property of atomic nuclei, has become a hotspot in quantum information technologies.^[8–10]

Metal complexes are versatile metalligand combinations, which consist of central metal atoms or ions and surrounding arrays of bound molecules or ions. Single-molecule magnets (SMMs), a special class of metal complexes with magnetic anisotropy and large spin moment, are one of the most promising magnetic molecules for exploring the quantum phenomenon involving spin at the nanoscale.^[11] SMMs combine the advantages of the molecular level with the characteristics of bulk magnetic materials, leading to high-density information storage.^[7] At low temperature, they exhibit magnetic bistability and extremely long magnetization relaxation times due to the significant energy

barrier of spin reversal.^[12,13] Furthermore, when scaled down to the single-molecule level, the spin behavior of molecular devices shows significant differences compared to bulk circuits, and the transport characteristics are also largely modified. Thus, understanding the spin behavior of SMMs at this level is crucial.

Single-molecule science focuses on the physical and chemical properties of single molecules and their interactions with the external environment.^[14,15] The embedding of SMMs into electronic devices has extensive applications in quantum computing and information storage, opening up an innovative research field of molecular spintronics.^[13] However, the realization of the precise manipulation and exert control of spin states in single-molecule devices is still challenging. With the development of technology over the years, a variety of methods have been developed to fabricate single-molecule spintronic devices, including mechanically controllable break junction (MCBJ),^[16] electromigration-fabricated break junction,^[17] scanning tunneling microscopy break junction (STM-BJ),^[18] lithography-defined cutting fabricated graphene-molecule-graphene single-molecule junctions (GMG-SMJs),^[19] and other approaches.^[20] These fabrication technologies employed in creating single-molecule spintronic devices provide a unique opportunity to explore single-spin behaviors that are inaccessible through conventional methods.^[21]

This review encapsulates recent research findings in the domain of spin of metal complexes and aims to provide a comprehensive overview of single-molecule spintronic devices. First, we highlight the importance of electron spin and nuclear spin, as well as the unique spin effects detected in single-molecule spintronic devices. Subsequently, we engage in a discussion on the regulation of electron spin and nuclear spin based on singlemolecule electronic devices, and briefly introduce the most exciting developments in this emerging field. Finally, the concluding remarks draw attention to the prevailing challenges and impediments in the realm of single-molecule spintronic devices incorporating metal complexes, emphasizing their pivotal importance for the future development of practical single-molecule spintronic devices based on metal complexes.

2. Electron Spin

When examining the characteristics of nanostructured systems through the lens of quantized energy levels, the spin degree of freedom invariably plays a pivotal role. The intrinsic motion of electrons, driven by their inherent angular momentum, was first conceptualized as electron spin by Samuel Goudsmit and George Uhlenbeck in 1925,^[22] and was introduced into quantum mechanics until 1928. Electron spin is a fundamental property of electrons, similar to charge. The recognition of the profound implications of electron spin was underscored by the 2007 Nobel Prize in Physics, awarded to Peter Grünberg and Albert Fert for their groundbreaking discovery of giant magnetoresistance (GMR), a phenomenon intricately associated with spindependent electron scattering, standing as a powerful affirmation of the immense potential in this field.

2.1. Electron Spin Effects

Electron spins at the molecular scale give rise to a myriad of fascinating quantum phenomena that have garnered considerable interest. The field of molecular spintronics is dedicated to harnessing the unique properties of single molecules as operational units for spintronic endeavors. This field pivots on the electron spin characteristics of these single molecules, offering a wealth of opportunities for the development of next-generation devices that leverage spin-dependent effects, such as Kondo effect, Zeeman splitting, spin crossover, and magnetoresistance effect.^[23] We will discuss one by one in the following subsections. Coulomb blockade and spin blockade play an important role in charge transport and spin manipulation for nanoelectronics,^[24–26] while they are rarely observed in metal complexes. Therefore, we do not discuss in the review.

2.1.1. Kondo Effect

The Kondo effect, initially observed in the 1930s in bulk metals with magnetic impurities, is distinguished by a reduction in electrical resistance at low temperatures.^[27] This phenomenon, characterized by an anomaly in resistance, was explained by Jun Kondo as resulting from the scattering of conduction electrons by these magnetic impurities.^[28] As depicted in **Figure 1**a, the conduction electrons' shielding of the magnetic moments of the impurities increases the effective scattering cross-section, thereby enhancing resistance.^[29] In the realm of molecular electronics, SMMs with non-zero spin exhibit a distinct zero-bias Kondo resonance in conductance, as seen in molecular electronic devices (Figure 1b,c).^[30] This resonance stems from the interplay between the central spins and the conductive electrons from the electrodes (Figure 1d),^[31] and the idealization model of such system was presented by Anderson in 1961.^[32]

The Kondo effect is measured by the Kondo temperature (T_k) , expressed as:^[33]

$$T_{\rm k} = 0.5 \left(\Gamma E_{\rm C}\right)^{1/2} \exp\left(-\pi\varepsilon/\Gamma\right) \tag{1}$$

where Γ is the level width caused by the tunnel coupling of molecules and electrodes, E_c is the charging energy, and ϵ is the difference between the localized electron and the Fermi energy of electrodes.

Enhancing the understanding of the Kondo effect's temperature dependence, Goldhaber-Gordon et al. proposed an empirical formula that more precisely captures the relationship:^[34]

$$(T,0) = \frac{G_0}{\left(1 + (2^{1/s} - 1)(T/T_K)^2\right)^s} + G_b$$
(2)

where G_0 and G_b correspond to the maximum conductance and background conductance, respectively, with s = 0.22 for the spin -1/2 Kondo effect.

Single-molecule devices serve as platforms for studying the Kondo effect, typically described as double barrier tunneling structure, where molecules are connected to the source and drain electrodes through contacts, with each contact acting as a tunneling barrier. It can be achieved through various methods. For instance, Zhao et al. investigated the differential conductivity of cobalt phthalocyanine (CoPc) molecules adsorbed on the surface of Au (111) using STM experiments.^[35] Initially, the absence of strong interaction between conductive electrons and cobalt ions precludes zero-bias resonance. However, after severing the ligand hydrogen atom with an STM tip pulse, the four orbitals of the d-CoPc chemically bond with the substrate, altering the molecular conformation and its coupling to the Au surface. This change leads to a modified interaction between molecular spins and conducting electrons, resulting in a discernible Kondo resonance (as shown in Figure 1e). Additionally, by fabricating closely spaced Au electrodes on an aluminum pad with a \approx 3 nm oxide layer

CIENCE NEWS



Figure 1. Kondo effect. a) Increase of effective scattering cross-section of magnetic impurities. Reproduced with permission.^[29] Copyright 2010, American Chemical Society. b) Splitting of the Kondo peak as a function of electrode spacing and c) dI/dV as a function of mechanical stretching. Reproduced with permission.^[30] Copyright 2010, American Association for the Advancement of Science. d) Correlation between the central spins and the conductive electrons leads to the formation of Kondo screening cloud. Reproduced with permission.^[31] Copyright 2022, Royal Society of Chemistry. e) Typical dI/dV spectra measured at the centers of CoPc and *d*-CoPc at different temperatures. Reproduced with permission.^[35] Copyright 2005, American Association for the Advancement of Science. f) Conductance versus bias voltage at various temperatures. Inset, the $\partial I/\partial V$ values plot as a function V_g . Reproduced with permission.^[36] Copyright 2002, Springer Nature.

serving as a gate electrode, reversible control of Kondo resonance through the gate voltage of a divanadium molecule was demonstrated (as depicted in Figure 1f).^[36]

2.1.2. Zeeman Splitting

Zeeman splitting, a pivotal quantum attribute of electron spin, emerges under the influence of an external magnetic field, effectively breaking the degeneracy of the spin-up and spindown states. This principle is harnessed in spintronic devices for applications in non-volatile memory storage and sensing technologies.^[33] For instance, a system with spin S = 1/2, which exists as a doublet with quantum numbers of $\pm 1/2$, experiences a separation into two distinct energy levels when subjected to a magnetic field. This interaction is captured by the Zeeman term H_z , which delineates the coupling between the spin *S* and the applied magnetic field *H*, expressed as:^[37]

$$H_z = g\mu_{\rm B}H \cdot S \tag{3}$$

where g denotes the g-factor, and $\mu_{\rm B}$ represents the Bohr magneton.

The Zeeman energy diagram provides a clear visualization of the Zeeman effect caused by an external magnetic field. In Figure 2a, the Zeeman energy diagram as a function of the external magnetic field for the $I = \pm 6$ ground state doublet of lanthanide single-ion SMMs is presented, clearly showing the splitting of the energies of the spin-split levels. As the intensity of the external magnetic field escalates, the separation between these two Zeeman effect-induced energy levels also increases. Figure 2b shows the enlargement of the region around zero field between the lowest substates.^[38] Notably, the $I = \pm 6$ substates achieve resonance at $\mu_n H = 0$ T, leading to an "avoided level crossing". This phenomenon facilitates quantum tunneling of magnetization (QTM), enabling magnetization reversal. Additionally, magnetization reversal can proceed through direct transition (DT), which involves the emission of phonons, especially under the conditions of stronger magnetic fields.^[39]

2.1.3. Magnetoresistance Effect

The magnetoresistance (MR) effect, a phenomenon where the electrical resistance varies with an applied external magnetic





Figure 2. Zeeman splitting. a) Zeeman energy diagram as a function of magnetic field. b) Enlargement of the region around zero field for the lowest J_z = 6 substates. Reproduced with permission.^[38] Copyright 2005, Wiley-VCH.

field, is a cornerstone in molecular spintronics. This variation is encapsulated by the magnetoresistance ratio (MR), calculated as: $^{[40]}$

$$MR = \frac{I_{\rm P} - I_{\rm AP}}{I_{\rm AP}}$$
(4)

where $I_{\rm P}$ and $I_{\rm AP}$ denote the total currents for parallel and antiparallel spin alignments, respectively.

Central to the field of molecular spintronics, one breakthrough in exploiting the magnetoresistance effect is single-molecule spin filters. These devices enable the selective transmission of electrons with a specific spin orientation, achieving a state of 100% spin polarization. This selective passage effectively transforms the molecule into an active spin filter, modulating the current flow in response to the magnetic field.^[41] The underlying mechanism of the modulation involves the expansion of density of states (DOS) of the molecule and an energy level shift,^[23] highlighting the nuanced interaction between molecular structure and spin behavior.

Given the huge potential of single-molecule spin filters, researchers are constantly exploring new molecular architectures to improve their performance. One promising direction is to incorporate SMMs into spin filters to achieve higher efficiency and responsiveness.^[42] In a notable study, Urdampilleta et al. demonstrated the integration of pyrene-substituted TbPc₂ molecules onto single-walled carbon nanotube (SWCNT) via $\pi - \pi$ interaction and connected between two palladium electrodes (Figure 3a).^[43] The transmission through the nanotube is influenced by the local magnetic moment of the pyrenesubstituted TbPc₂ molecules, and its orientation is controlled by an external magnetic field (Figure 3b). Experiments based on such devices reveal conductance switches between highand low-resistance, which can be tuned via an external magnetic field (Figure 3c). The strong magnetoresistance of up to 300% below 1 K by reversing the magnetic field allows for the electrical detection of magnetization switching. Besides, Díez-Pérez and co-workers investigated spin filter behavior of the paramagnetic $[Fe(tzpy)_2(NCX)_2]$ (X = S and Se, tzpy = 2pyridyl[1,2,3]triazolo[1,5- α]pyridine) complex and the diamagnetic $[FeL^{A}(NCS)_{2}]$ (L^A = N,N'-bis(1-pyridin-2-ylethylidene)-2,2dimethylpropane-1,3-diamine) complex at room temperature,

when connected between the magnetically polarized Ni tip and the Au substrate in STM measurements (Figure 3d).^[44] As depicted in Figure 3e, once the polarization of the ferromagnetic Ni tip changed from spin α -up to spin β -down, the conductance of the high-spin (HS) Fe²⁺ state in [Fe(tzpy)₂(NCX)₂] at near-zero bias voltage will increase 100 times. In contrast, the low-spin (LS) Fe²⁺ state in [FeL^A(NCS)₂] complex remains invariable irrespective of the Ni polarization (Figure 3f). Furthermore, the Cu substrate does not exhibit such spin-polarized transport performance, which emphasizes the role of spin–orbit coupling at Au–S interface in the generation of polarized electrons.

Moreover, the anisotropic magnetoresistance can be modulated between two molecular orbitals through spin–orbit coupling. Gao et al. observed an effectively tunable giant magnetoresistance using STM technique with the influence of an external magnetic field.^[45] Under the weak magnetic field, the transmission path of electrons is prone to the d_{xz}/d_{yz} orbital, and the Fe spin direction is in the plane. As the external magnetic field increases, electrons flow by the d_{z^2} orbital and the Fe spin direction is aligned with the external magnetic field, resulting an anisotropic magnetoresistance of up to ≈93%.

2.2. Spin Crossover Related Electron Spin Manipulation

Achieving reversible spin manipulation at the single-molecule level stands as a coveted objective in molecular spintronics and represents a captivating application for electron spin in the realm of quantum information processing.^[46] The phenomenon of spin crossover (SCO) occurs within certain metal complexes and some SMMs, where the spin states are modulated by external stimuli, including temperature, light, magnetic fields, and electric fields. It is commonly divided into two categories: physical and chemical factors.^[47]

SCO molecules generally feature transition metal centers with electronic configurations ranging from $3d^4$ to $3d^7$, set within an octahedral geometry.^[48] The ligand field theory posits that the five d orbitals of these metals split into two distinct energy levels— t_2 g and e_g —due to ligand repulsion, with the splitting energy (Δ) escalating as the ligand field strengthens. In the case of octahedral transition metals with $3d^4$ – $3d^7$ configurations, the electronic arrangement is determined by the interplay between the

IENCE NEWS



Figure 3. Single-molecule spin filters. a) Scheme of the supramolecular spin filter architecture involving two TbPc₂ molecules grafted on an SWCNT. b) Schematic representation of the magnetoresistance behaviors of two TbPc₂ molecules. c) Zero-bias conductance versus the magnetic field under increasing and decreasing fields. Reproduced with permission.^[43] Copyright 2011, Springer Nature. d) Schematic representation of the single-molecule junctions by bridging Fe^{II} SCO complexes between gold electrode and magnetically polarized nickel electrode. e) Conductance histograms of [Fe(tzpy)₂(NCS)₂] and f) [FeL^A(NCS)₂] under different Ni magnetic polarizations. Reproduced with permission.^[44] Copyright 2016, American Chemical Society.

splitting energy and the pairing energy (*P*). For instance, with a strong-field ligand surrounding an octahedral Fe²⁺ ion, the splitting energy Δ surpasses the pairing energy *P*, prompting the six *d* electrons to pair up, resulting in a LS state. Conversely, in the presence of a weak-field ligand, the splitting energy Δ falls below the pairing energy *P*, leading electrons to occupy orbitals separately, forming a HS state in accordance with Hund's rule (**Figure 4a**). When the splitting energy Δ is comparable to the pairing energy *P*, external influences can toggle the spin states, manifesting SCO behavior.^[49] The profound alterations in the physical properties of these molecules, triggered by such spin transitions, render SCO molecules exceptionally promising for the development of future molecular devices.

2.2.1. Physical External Stimuli

Physical external stimuli are potent inducers of SCO behavior in single molecules, offering a versatile toolkit for manipulating molecular spin states. Generally, temperature induction is a commonly used method, and HS state is stable at higher temperatures, while LS state prefers lower temperatures. The SCO temperature ($T_{1/2}$) is defined as the temperature at which the HS and LS states have the same proportion and is used to evaluate the SCO effect.^[50] Apart from temperature induction, the spin state of a single molecule can also be converted from LS to HS by light, in which the SCO can be triggered by a light-induced excited spinstate trapping (LIESST) process. In the LIESST process, a multistep mechanism involving several excited spin states has been proposed. The corresponding process starts from the LS singlet ground state, excites to an intermediate/metastable spin state, and finally becomes trapped in the HS state. Such transition can be triggered reversibly by heat or light.^[48]

In addition to temperature and light, mechanical manipulation presents another avenue for SCO induction of a single molecule. As displayed in Figure 4b, Lin et al. have harnessed the STM-BJ technique to alter the spin state of Fe-porphyrin by mechanically stretching or squeezing. When raising the tip height, the molecular conformation changes from saddle to planar, resulting in a spin state switch from S = 2 to S = 1, as reflected in the conductance measurements (Figure 4c). This is due to the variation in the Fe–N bond length: the intermediate spin state (S = 1) as the ground state in gas phase has a shorter bond length. Meanwhile, the spin state of the center Fe²⁺ ion changes reversibly from LS to HS state upon mechanical compression.^[51]

The modulation of electron spin states in SMMs through electrostatic gating is of paramount importance. The single-molecule field-effect transistor (FET) provides an ideal method for electric field-based spin state regulation of SMMs. For instance, the transition from an HS ground state (S = 5/2) to an LS state (S = 1/2) in a Mn^{2+} complex-based three-terminal molecular spin transistor is facilitated by the gate electric field (Figure 4d).^[52] This

CIENCE NEWS

Small methods www.small-methods.com



Figure 4. Physical external stimuli induced spin crossover. a) Schematic diagram of SCO for octahedral Fe²⁺. Reproduced with permission.^[49] Copyright 2020, MDPI. b) Chemical structure of the Fe-porphyrin molecule. c) *dI/dV* of one junction undergoing multiple tip upward and downward cycles. Reproduced with permission.^[51] Copyright 2017, American Chemical Society. d) Molecular structure of the Mn²⁺ complex, showcasing two distinct *d*⁵ electronic configurations of the Mn²⁺ core. Reproduced with permission.^[52] Copyright 2010, American Chemical Society. e) Electric field-induced spin crossover based on the Stark splitting. Reproduced with permission.^[54] Copyright 2014, American Physical Society. f) Schematic representation of the voltage-triggered SCO effect. Reproduced with permission.^[55] Copyright 2015, Wiley-VCH. g) Switchable spin devices created by the MCBJ technique. h) Bistable *I–V* curves and (i) differential conductance of the coupled spin pair. Reproduced with permission.^[56] Copyright 2013, Springer Nature.

transition occurs as the increased gate voltage adds an electron to the ligand, thereby enhancing the ligand field and coupling strength between the Mn²⁺ complex and ligands, driving the spin state from HS to LS.

Moreover, Stark splitting, the splitting of degenerate energy levels under an external electric field, presents another avenue for electron spin manipulation.^[53] The idea behind spin-dependent Stark effect is the crossing of high-spin and low-spin levels in a single-molecule device. In general, the high-spin and low-spin states of molecules with different permanent electric dipole moments have different energies, which means that the energy barrier between the two spin levels can be compensated by the action of an applied electric field (Figure 4e).^[54] This inspires us to achieve the spin quantum state selectivity by controlling the Stark effect. By using MCBJ technique, Mayor et al. investigated the voltage-triggered spin manipulation of Fe²⁺ terpyri-

dine molecule.^[55] As shown in Figure 4f, when there is no external stimulus, the two terpyridine ligands are arranged vertically to each other, and the central Fe²⁺ ion is in the LS state (S = 0). By applying an appropriate bias voltage, the terpyridine ligands rotated for a certain angle, forming a reduced ligand field. Thus, the electron spin changes from LS to HS state (S = 2). Weber et al. further investigated a bias-induced repeated spin switch of a Co²⁺ molecule between the pseudosinglet state and the pseudo-triplet state (Figure 4g).^[56] The authors claimed to detect a coupled spin pair confined in a single molecule and the switch between two states. As shown in Figure 4h, bistability can be observed on a single curve and these two correlated data can be interpreted as a switch from the non-magnetic pseudo-singlet state (type II) at low bias to the magnetically active pseudo-triplet state (type I) at high bias (Figure 4i).





Figure 5. Chemical regulation of spin crossover. a) The molecular levels involved in the reaction between NO and CoTPP. b) Schematic diagram of the switching process. Reproduced with permission.^[58] Copyright 2010, Springer Nature.

2.2.2. Chemical External Stimuli

Beyond the realm of physical external stimuli, chemical regulation emerges as a potent alternative for manipulating the spin state of a single molecule. Through the strategic modification of organic ligands, the ligand field can be directly manipulated, leading to substantial changes in the properties that govern SCO behavior.^[57] This approach allows for the precise adjustment of the molecular environment, effectively sculpting the SCO characteristics. In addition to modifying ligands, the formation of new chemical bonds offers a complementary strategy for fine-tuning SCO behavior. A prime example is the interaction of cobalt (II) tetraphenylporphyrin (CoTPP) with Ni substrates, where the system is initially in a HS state (S = 1/2). The introduction of nitric oxide (NO) molecules triggers a coupling between the unpaired electron of CoTPP and the π -electron of NO, resulting in the formation of a NO-CoTPP complex and a concomitant shift to a LS state (S = 0) (Figure 5a). Notably, heating the system to release the NO molecule facilitates a return to the original HS state (Figure 5b).^[58]

Furthermore, the SCO behavior can be adeptly manipulated by chemically modifying counterions, solvents, and guest molecules, enabling a flexible switch between the two spin states.^[57] Such chemical modulation not only broadens the scope of SCO applications of a single molecule but also underscores the versatility of chemical interventions in the realm of spin state modulation.

3. Nuclear Spin

Nuclear spin, a fundamental property stemming from the internal motion of the atomic nucleus, represents the vector sum of its internal spin and orbital angular momentum. In a seminal development in 1924, Pauli introduced the concept of nuclear spin, drawing on observations of the hyperfine structure within sodium spectra.^[59] The study of nuclear spin mainly involves the characteristics of spin and their interactions, which play an important role in modern physics. This research is pivotal for advancing our comprehension of the stability and intricate inner workings of atomic nuclei. It sheds light on the complex interplay between atomic nuclei and elementary particles, thereby enhancing our grasp of nuclear spin's potential applications and harnessing its capabilities for future technologies. The exploration of nuclear spin not only deepens our understanding of the quantum world but also opens avenues for innovation in nuclear physics and spin-related disciplines.

3.1. Nuclear Spin Coupling

For simple physical models, the study of electronic energy states in atoms and molecules typically simplifies the atomic nucleus to a positively charged entity, while often ignoring the subtle but significant effects of nuclear spin. It is crucial to recognize that nuclear spin possesses the capacity to alter the energy states of electrons in orbit around the nucleus, thereby affecting the intrinsic properties of atoms and molecules. Specifically, nuclear spin can interact with electron spin through its magnetic moment, with the strength of this coupling being determined by a variety of intrinsic factors such as inter-nuclear distance, nuclear magnetism, and molecular structure. In the context of single-molecule research, incorporating the effects of nuclear spin coupling is of paramount importance. It enables researchers to elucidate the energy structures and provide more accurate explanations of physical properties such as molecular emission spectra, enriching our understanding of the quantum behavior at the molecular level.

3.1.1. Concept of Nuclear Spin

Nuclear spin, an intrinsic property of atomic nuclei, represents the fundamental physics of the total angular momentum *I* of a nucleus.^[59] Atomic nuclei, made up of protons and neutrons, exhibit nuclear spins for each constituent with an electron spin parallel, each having a spin quantum number S = 1/2. Distinct from electron spin, the nuclear spin often manifests as a unified entity, encompassing both spin and orbital angular momentum components. The nuclear magnetic moment, although significantly smaller than its electronic counterpart, is instrumental in magnetic interactions with the surrounding environment.^[60] A nucleus with spin *I* can assume 2I + 1 distinct orientations, with its energy levels splitting in the presence of a magnetic field or during photon absorption or emission. Each level, defined by a quantum number, underscores the nuclear spin as a pivotal identifier of nuclear energy levels.^[61]

The study of nuclear spin wields profound implications for the physical and chemical properties of matter, rendering the determination of spin states a critical facet of research within this domain. A plethora of techniques exist for measuring spin, with atomic spectroscopy and nuclear magnetic resonance (NMR) emerging as two of the most efficacious methods.^[62,63] Atomic spectroscopy capitalizes on the hyperfine structure within atomic emission spectroscopy to ascertain the spin of atomic nuclei, utilizing electromagnetic radiation to excite the nuclei and subsequently deciphering the atomic radiation lines to observe the energy level splitting peaks stemming from the coupling of electron and nuclear angular momenta. Conversely, NMR leverages the precession motion of the nuclear magnetic moment, induced by the spin of atomic nuclei in an external magnetic field, to ascertain nuclear spins (Figure 6a). The quantized precession energy, as dictated by quantum mechanics, signifies discrete magnetic moment energy levels. When a nucleus absorbs radiofrequency energy resonant with its precession frequency, transitions between nuclear spin energy levels ensue, culminating in the amplification of nuclear spin into observable NMR signals (Figure 6b).

However, these classical techniques, while robust for macroscale material systems, falter in characterizing nuclear spin information at the single-molecule level. Single molecules, as the quintessential quantum units, offer an unprecedented vantage point for the precise investigation of nuclear spin-related properties, enabling the direct extraction of key parameters such as the coherence lifetime and relaxation time of nuclear spin. This approach paves the way for novel trajectories in fundamental physics research and is anticipated to catalyze significant advancements in the realms of nuclear spin manipulation and quantum information storage.

3.1.2. Hyperfine Interaction

The hyperfine interaction stands as a pivotal element within the realm of atomic physics, particularly in the analysis of nuclear

reactions and nuclear spin effects.^[64] This interaction can lead to the splitting of energy levels, subsequently altering the characteristics of nuclear radioactive decay. In the tapestry of atomic and molecular physics, the hyperfine interaction has emerged as a key factor in explaining hyperfine structure in the spectrum and revealing fundamental physical processes.^[65,66] The hyperfine interaction is bifurcated into two principal mechanisms: the electric quadrupole interaction, stemming from the nuclear quadrupole moment within an electric field, and the magnetic dipole-dipole interaction, arising from the nuclear magnetic moment within a magnetic field. These interactions introduce minor additional energy into atoms, leading to the further splitting of atomic energy levels. Consequently, such splitting gives rise to additional spectral lines that are extremely close to the original atomic spectral lines on the energy spectrum, ultimately creating compact and ultrafine atomic spectral structures. Among the interactions, the hyperfine interaction of magnetic dipoles has been extensively investigated.^[67–69] It is characterized by the coupling between the nuclear and electronic spins through their respective magnetic moments, thereby influencing the energy state of electrons external to the nucleus and engendering the hyperfine interaction energy. When viewed through the lens of angular momentum, the potential allowable states of the hyperfine interaction energy can be deduced. The orbital angular momentum L of the electron, when coupled with its spin angular momentum S, culminates in the total angular momentum J. This J, when intertwined with the total angular momentum I of nuclear spin, births the total angular momentum of atom, denoted as F. The interplay of angular momenta is encapsulated by the following relationships:

$$L + S = J \tag{5}$$

$$J + I = F \tag{6}$$

The magnitude of the total angular momentum vector *F* is articulated by the expression:

$$F = \sqrt{f(f+1)}h\tag{7}$$

The total angular momentum quantum number f can be defined as f = j + i, j + i - 1, \cdots , |j - i|, with the total number of values for f is 2i + 1 when i < j or 2j + 1 when j < i. The orientation of F is subject to spatial quantization, with its projection in the *z*-direction adhering to the equation:

$$F_z = m_f h \tag{8}$$

 m_f represents the magnetic quantum number of the total angular momentum, and $m_f = f, f - 1, \dots, -(f - 1), -f$, which have 2f + 1 possible values. The energy of the hyperfine interaction, V_{HFS} , manifesting from the interplay between the magnetic field generated by the electrons, B_j , and the nuclear magnetic moment μ_i , is articulated as:

$$V_{\rm HFS} = -\mu_{\rm i} \cdot B_{\rm j} = -\frac{g_{\rm j}\mu_{\rm N}}{h}I \cdot B_{\rm j}$$
⁽⁹⁾

$$\mu_{\rm i} = g_{\rm i} \mu_{\rm N} \frac{I}{h} \tag{10}$$

CIENCE NEWS



Figure 6. Basic concepts and phenomena of nuclear spin. a) Larmor precession of the nucleus in the external magnetic field. b) Projection of the nuclear spin. c) Vector relationship among the three angular momenta *I*, *J*, and *F* in space. d) Energy level splitting after hyperfine interaction of atomic orbitals. e) The QTM structure between two energy levels of SMMs. Reproduced with permission.^[82] Copyright 2013, American Physical Society. f) Classical Einstein–de Haas experiment. g) TbPc₂ connected in the CNT mechanical resonator through π – π interaction. h) Zeeman diagram of the ground state energy levels of the TbPc₂ molecule. i) Direct transitions of the four spin states at different magnetic field intensities, which makes significant jumps of the conductance of the CNT resonator. j) Schematic diagram of the direct transition corresponding to the electron spin reversal. Reproduced with permission.^[80] Copyright 2016, Springer Nature.

In these equations, g_i is the g-factor of the atomic nucleus, and the relationship between nuclear magneton μ_N and Bohr magneton μ_B is $\mu_N \approx \frac{\mu_B}{1836}$. Given that B_j is antiparallel to *J* and proportional to it, Equation (9) can be reformulated in terms of *I*–*J* coupling:

$$V_{\rm HFS} = -\mu_{\rm i} \cdot B_{\rm j} = g_{\rm i} \mu_{\rm N} \frac{I}{h} \cdot \frac{J}{|J|} B_{\rm j}$$
$$= \frac{g_{\rm i} \mu_{\rm N} B_{\rm j}}{\sqrt{j (j+1)}} \frac{I \cdot J}{h^2} = \frac{a}{h^2} I \cdot J = AI \cdot J$$
(11)

Here, *a* and *A* represent the magnetic hyperfine constant and the magnetic hyperfine interaction constant, respectively, with

 $a = \frac{g_i \mu_N B_j}{\sqrt{j(j+1)}} = Ah^2$ and $|J| = \sqrt{j(j+1)}h$. The conservation relationship among *I*, *J*, and *F* in space is depicted as a vector triangle, as illustrated in Figure 6c. By applying the cosine theorem, the following relationship is derived:

$$|F|^{2} = |I|^{2} + |J|^{2} + 2|I||J|\cos(I,J)$$
(12)

Through Equation (12), it can be obtained that:

$$I \cdot J = |I| |J| \cos (I, J) = \frac{1}{2} (|F|^2 - |I|^2 - |J|^2)$$
$$= \frac{h^2}{2} [f (f+1) - i (i+1) - j (j+1)]$$
(13)

For Equation (11), $V_{\rm HFS}$ can be further expressed as:

$$V_{\rm HFS} = -\mu_{\rm i} \cdot B_{\rm j} = \frac{a}{h^2} I \cdot J = \frac{a}{2} \left[f \left(f + 1 \right) - i \left(i + 1 \right) - j \left(j + 1 \right) \right]$$
(14)

From Equation (14), the number of the potential allowable states of V_{HFS} is determined by the *f*, which can be 2j + 1 when j < i or 2i + 1 when i < j (Figure 6d). This confirms that each level of V_{HFS} exhibits a degeneracy of 2f + 1.

The exploration of hyperfine interaction at the single-molecule scale is primarily evident in its role in instigating significant shifts within quantum phenomena. For instance, Zheng et al. investigated the quantum tunneling mechanism based on $[Dy(tBuO)Cl(THF)_5][BPh_4]\cdot 2THF$ SMM and discovered that the interplay of hyperfine interaction can adeptly manipulate and widen the tunneling gaps, thereby modifying the tunneling probability of single-molecule magnets.^[70] Additionally, the hyperfine interaction is intricately associated with spin-lattice relaxation and quantum coherence. Examining the interaction at the single-molecule scale can open an avenue for exploring the intrinsic properties of quantum physics at the microscopic scale, potentially offering insights for the functional design and construction of molecular devices.

3.2. Nuclear Spin Effects

Although significant breakthroughs and applications have been made in nuclear spin-related research at the macroscopic scale, the study of nuclear spin effects at the single-molecule scale can provide new avenues for exploring rich quantum phenomena. The nuclear spin effects can cause molecules to form unique energy-level structures that facilitate electron transitions or tunneling under the external field. In addition, this process may also involve changes in spin states, providing numerous opportunities for the further development of novel spintronic devices and coherent spin manipulation techniques. Next, we will discuss relevant quantum phenomena at the single-molecule scale, in which the molecular energy states are governed by the introduction of nuclear spin effects.

3.2.1. Quantum Tunneling of Magnetization

The tunneling effect, a quintessential quantum mechanical phenomenon, encapsulates the remarkable ability of microscopic particles to transcend energy barriers that exceed their own total energy.^[71,72] The probabilistic traversal of these barriers, underpinned by the wave-like nature of particles, diverges from classical expectations, allowing particles to penetrate rather than being wholly reflected. This quantum behavior is not merely a theoretical curiosity but a pivotal force across various scientific disciplines.

In the realm of semiconductor technology, tunneling profoundly influences electron transport, thereby sculpting the performance of semiconductor devices. Similarly, within the domain of magnetic metal complexes, the tunneling effect facilitates the low-temperature reversal of magnetization in certain materials, an instance of macroscopic QTM.^[73–75] The genesis of the exploration of QTM dates back to 1986, when Uehara et al. observed a step-like magnetization jump in SmCo_{3.5}Cu_{1.5} below 2 K, marking a seminal moment in QTM research.^[76] The subsequent discovery of SMMs propelled QTM into a research hotspot,^[74,75,77,78] given that the hyperfine interactions within these SMMs, stemming from the nuclear spin of rare-earth ions, can notably modulate electron energy states and the tunneling energy gap.

QTM refers to the phenomenon that when the energy difference between the magnetic levels of a magnetic system is less than the tunnel splitting energy, the magnetization intensity can undergo resonant quantum tunneling between different magnetic levels. It manifests as a regular step change in macroscopic magnetization intensity with the external magnetic field. Delving into QTM within SMMs enriches our fundamental physics understanding and lays a solid foundation for the construction of diverse microelectronic devices. For instance, magnetization sensors leveraging the QTM effect can detect subtle magnetic field variations, and integrated SMMs may pave the way for new storage and computing devices.

The investigation of QTM at the single-molecule scale is crucial for understanding its intrinsic properties and elucidating its regulatory mechanisms. A paradigmatic example is the TbPc₂ system, integrable within nanoscale electrode gaps to form a molecularly bridged transistor device.^[39,43] Capitalizing on this robust device platform, single-molecule QTM observations have been achieved, as depicted in Figure 6e. The nuclear spin of central atom of TbPc2 and electron spins, through hyperfine interaction, create a tiered energy landscape split into closely spaced levels, endowing it with a substantial QTM propensity. External fields, particularly magnetic fields, can adjust the energy barriers, thus manipulating the QTM. In other words, the magnetic field can effectively change the magnetic anisotropy barrier between the two energy states, allowing tunneling to occur between spin electrons in the lowest barrier state, and this process accompanies spin-state inversion. Beyond magnetic fields, an array of non-magnetic methods is being harnessed to control QTM in SMMs, offering innovative pathways for quantum bit construction and the realization of quantum computing with single molecules, and driving forward the innovation in information science.

3.2.2. Quantum Einstein-de Haas Effect

Over a century ago, Einstein and de Haas unveiled a remarkable phenomenon: the application of a current pulse to a coil induces mechanical rotation in a ferromagnet. This discovery provided a direct experimental means to explore the interplay among magnetic fields, angular momentum, and the spin of elementary particles.^[79] The classical Einstein–de Haas experiment illustrates that changes in the magnetization of a macroscopic magnet are accompanied by mechanical rotation, as depicted in Figure 6f. This phenomenon is a macroscopic manifestation of the conservation of total angular momentum and energy at the atomic level. Consider an object composed of *N* atoms of magnetic moment $M = N\gamma_J J$, where γ_J is the gyromagnetic ratio and J = L + S represents the total angular momentum of an atom. The total angular momentum of the magnet suspended from a string is a sum

of mechanical orbital moment Γ originated from the rotation of the object and $N\langle J\rangle$. $N\langle J\rangle$ refers to the sum of spin and orbital angular momentum of the object composed of *N* atoms. If the object originally at rest and nonmagnetized, generates a macroscopic magnetic moment, and the conservation law requires that $N\langle J\rangle + \Gamma = 0$. This implies $\Gamma = -M/\gamma_J$, indicating that the object begins to rotate upon magnetization.

However, for an intuitive grasp of this mechanism, one must look to the quantum level, examining single-spin systems such as individual atoms or molecules. The investigation of the Einsteinde Haas effect at the single-molecule level is of immense significance, as it sheds light on the fundamental physics of angular momentum conservation and holds vast potential for applications in molecular quantum spintronics. Recent experiments have successfully characterized the Einstein-de Haas effect at the singlemolecule level, confirming the conservation of total angular momentum and energy. For instance, Ganzhorn et al. connected a SMM with pronounced hyperfine interactions to a carbon nanotube mechanical resonator via $\pi - \pi$ interactions (Figure 6g).^[80] The Tb³⁺ ion, nestled between two planes of Pc ligands, is central to spin reversal due to its strong spin-orbit coupling, resulting in a magnetic ground state with I = 6. The Tb³⁺ ion, with a nuclear spin quantum number of 3/2, interacts strongly with the electron spin state via hyperfine interaction, splitting the ground state energy level into four distinct states (Figure 6h). When subjected to a magnetic field, these four states of the molecule can potentially undergo two distinct spin-state transitions. Theoretically, for weaker external magnetic fields, the energy barrier between the upper and lower spin states is minimal, allowing for QTM and spin reversal without external energy. However, as the magnetic field strength increases, the energy barrier escalates, rendering QTM incapable of overcoming the barrier, and direct transitions become necessary with the aid of external energy (Figure 6h,i).^[81]

Interestingly, in their experiments, no spin reversal signals were detected in the lower magnetic field region, and significant transition signals emerging only in the higher magnetic field region. This indicates that the QTM process is completely suppressed, and only direct transition processes occur. Theoretically, this selective spin-state reversal adheres to the conservation of energy and momentum. The spin reversal via QTM in TbPc2 generates a quantized phonon mode with an energy of 1 µK, whereas direct transitions produce a phonon mode with an energy of 1.5 K (Figure 6j). The weak phonon mode cannot match the energy required for the mechanical rotation of the single-molecule magnet confined within the carbon nanotube resonator, thus inhibiting the QTM process. In contrast, the energy of direct transition aligns effectively with the magnitude of energy of the longitudinal phonon mode for the rotation of the SMMs around the magnetic easy axis. During spin reversal, the molecule rotates by exchanging phonon energy of equal magnitude.

The study of the Einstein–de Haas effect in special SMMs with hyperfine interaction not only corroborates the fundamental physical principles at the quantum level but also demonstrates the robust effect against changes in phonon energy. This implies that molecular spins can be effectively shielded from quantum fluctuations, providing valuable insights into achieving coherent spin manipulation at the single-phonon level.

3.3. Nuclear Spin Manipulation and Applications

Since the pioneering discovery of nuclear spin, physicists have been at the forefront of endeavors to effectively manipulate and interpret its quantum behavior. The early employment of magnetic fields to control atomic nuclear spin was instrumental in the development of NMR technology, a milestone that has not only unraveled the intricate chemical structures of materials but also revolutionized the field of medical diagnostics and therapeutics.^[83] As the field progressed, innovative methods for nuclear spin manipulation began to surface, including the utilization of microwaves and electric fields to modulate and decipher the quantum information encoded within nuclear spins.^[84,85] These advancements have propelled the evolution of spin-based qubits and the realm of quantum computing, offering a robust foundation for the next generation of computational technologies.

3.3.1. Concept of Nuclear Spin Manipulation

In contemporary research, quantum computation harnessing the manipulation of nuclear spins has emerged as a trending subject within the information sciences domain. The primary focus of this research is on solid-state materials, with a particular emphasis on incorporating specific atomic species into these materials.^[9,86–89] For instance, the integration of ³¹P atoms into silicon substrates is a well-established practice.^[9,89] Once incorporated, the nuclear spin states of ³¹P are amenable to encoding and manipulation.

Nuclear spins are characterized by their extended coherence times, which provide superior resilience against environmental interferences, even within complex settings. This inherent quality is advantageous for the non-destructive and coherent manipulation and measurement of nuclear spin quantum states, thereby enhancing their viability for practical applications. To date, the manipulation of nuclear spins within solid materials has reached a sophisticated level of development.

Nevertheless, the task of precisely controlling and reading nuclear spin states at the single-molecule level presents a formidable challenge. Overcoming this challenge is crucial for propelling quantum computing forward. The advent of SMMs has ignited hope for the development of quantum information units, offering a promising avenue for constructing and manipulating qubits. In the past decade, quantum computing research anchored in SMMs has witnessed a cascade of break-throughs, spanning from device fabrication to the adept readout of spin quantum information and the execution of precise coherent manipulation techniques.^[90–92] These advancements have sparked innovative concepts that could facilitate the transition of quantum computing from theoretical constructs to tangible applications.

3.3.2. Manipulation of Nuclear Spin Qubits

Processing information at the quantum level and the realization of quantum computation represent the confluence of scientific and technological advancement at the nexus of physics

CIENCE NEWS



Figure 7. Manipulation of nuclear spin. a) Construction of a single-molecule transistor. b) Readout of the spin states through the electrical method. c) The upper panel shows the Zeeman diagram of the ground state energy levels of single TbPc₂ molecule. The lower panel shows the significant jump in the conductance of single TbPc₂ molecule transistor. d) Rabi oscillations of the qubits built with the nuclear spin states between $| + 1/2 \rangle$ and $| + 3/2 \rangle$. Reproduced with permission.^[91] Copyright 2014, American Association for the Advancement of Science.

and computer science. A pivotal component of this quantum leap is the construction of fundamental information units known as qubits, which can usually be photons, spins, etc.^[93–96] The advent of quantum computation leveraging nuclear spin qubits has propelled the development of nanoscale SMM transistors.^[90] These spin-based qubits have achieved significant breakthroughs in the realms of information encoding, coherent manipulation, and reading, thereby charting a course for the advancement of nanoscale quantum algorithmic devices.^[90,91,97]

Recently, Thiele et al. connected the TbPc_2 to the gap between gold nanoelectrodes through the electromigration technique, constructing a single-molecule transistor based on nuclear spin states, and achieving coherent operation and reading of nuclear spin quits, as illustrated in **Figure** 7a,b.^[90] The central Tb³⁺ ion, with its electron's spin angular momentum quantum number totaling 6, is shielded by two Pc ligands that generate a protective ligand field, preserving the spin coherence of the Tb³⁺ ion. Moreover, the Tb³⁺ ion, which has a nuclear spin quantum number of 3/2, couples with the electron spin through hyperfine interaction, splitting each electron spin ground state into four different quantum states (see Figure 7b). By modulating the strength of magnetic field, these coupled spin states can undergo QTM, precipitating a reversal in magnetization of electron spin. This phenomenon is detectable as a significant current jump at the spin reversal point, measured across the transistor's source and drain electrodes. Since the variation in the magnetic field required for electron spin reversal varies with different nuclear spin quantum numbers, the corresponding nuclear spin states can be distinguished based on changes in the conductance signal under different magnetic fields, as depicted in Figure 7c. Nuclear spin states can be initialized by adjusting the magnetic field to a specific magnitude, paving the way for subsequent spin manipulation. To achieve this, Rabi oscillations between two nuclear spin states, exemplified by I = +1/2 and I = +3/2, are employed to forge a qubit. The electric field, with its tunability and capacity for localized focus and shielding in confined spaces, presents an optimal and accessible means of control. This manipulation strategy, implementable via microwave (MW) radiation, addresses the bottleneck of parasitic crosstalk between adjacent spin qubits. Initially, the magnetic field is fixed at the $| + 3/2 \rangle$ state for initialization. Subsequently, a MW pulse, characterized by a specific frequency n_0 and duration τ , is applied to the transistor. According to the hyperfine Stark effect, the electric field of the microwave pulse can be converted into a local magnetic field. Besides, the hyperfine Stark effect describes the change of the hyperfine constant A in the Hamiltonian $H_{\rm HF} = AI \cdot J$ as a function of the external electric field, and A can be converted into a change in the effective magnetic field *B* at the center of the atomic nucleus. Consequently,

the MW pulse instigates an oscillating magnetic field, engendering Rabi oscillations between the $| + 1/2 \rangle$ and $| + 3/2 \rangle$ states of the nuclear spin, thereby constructing a superposition of qubits as shown in Figure 7d. Ultimately, the final state of nuclear spin qubits corresponding to the electron spin reversal point can be read out under the scanning of the external magnetic field.

In addition, achieving efficient manipulation of qubits also requires precise acquisition of their coherence time, T_2 , as environmental noise may cause rapid decoherence (i.e., fail to maintain the original state). The T_2 is usually determined by pulse sequence in optics or magnetic resonance, such as Hahn echo and Ramsey interference. The measurement begins with determining the initial state. For instance, in an energy level system consisting of $|+1/2\rangle$ and $|+3/2\rangle$ states, it is assumed that the initial state is fixed at $| + 1/2 \rangle$. By applying a $\pi/2$ time-domain microwave pulse, qubits are prepared into their superposition states, and the superposition state accumulates the phase during an evolution time *t*. Then, a second $\pi/2$ time-domain microwave pulse is applied to convert the evolution results into the final measurement state. At this point, the electrical signals of the singlemolecule device are immediately tested to read the final $|+3/2\rangle$ state. By repeatedly counting the results of this step and recording the decay curve of the probability of the final state occurring within the evolution time *t*, the coherence time can be presented.

The precise and coherent manipulation of nuclear spin qubits in single-molecule magnets, empowered by MW pulse-based electric fields, has laid a common pathway for the evolution of spin quantum nanodevices. Furthermore, it has propelled forward the cutting-edge technologies of quantum computing and quantum sensing, infusing robust momentum into their development.

3.3.3. Implementation of Quantum Algorithm

The realization of practical quantum computing requires not only the construction of qubits, but also the creation of quantum algorithms for information processing.^[97,98] An algorithm, by definition, is a systematic strategy for tackling specific computational challenges. Essentially, a quantum algorithm employs a sequence of operators on an initial quantum state, resulting in a final state that encodes the solution to a problem.^[99] These algorithms are versatile, capable of addressing complex computational tasks such as optimization, simulation, encryption, search operations, and the resolution of linear equation systems.^[100] The crafting of qubits and the finesse of algorithm manipulation together form the bedrock of advanced parallel computing paradigms.

Over the past two decades, the field of quantum computing, underpinned by SMMs, has made the journey from theoretical constructs to tangible experimental milestones.^[37,101] In a landmark 2001 theoretical proposal, it was suggested that the Grover algorithm, renowned for its efficiency in searching unsorted databases, could be harnessed using SMMs.^[37] It first constructs a Hadamard gate to create a coherent superposition state, and after iterations, the superposition system evolves to the desired state with very high probability. The Hadamard gate, a fundamental logical gate, creates an equal probability distribution in the allowed states. The Grover algorithm's unique advantage lies in its capacity to manipulate multiple states in unison without necessitating quantum entanglement, thereby achieving its computational objectives.

The multi-level system of nuclear spin in SMMs is well suited for simple computations based on the Grover's algorithm. For example, Godfrin et al. demonstrated the use of microwaves to manipulate the TbPc2, thereby endowing it with search capabilities.^[101] The four nuclear spin states of this molecule have unequal energy level spacings, resulting in different resonance frequencies for different energy level transitions, respectively (as shown in Figure 8a). These frequencies, falling within the microwave spectrum, enable the induction of Rabi oscillations through microwave pulses tuned to these specific frequencies, thereby constructing multi-level qubits. From the perspective of quantum mechanics, microwave pulses act as unitary operators on spin wavefunctions, with multiple pulses of varying frequencies driving the evolution of different spin wavefunctions simultaneously. This time-dependent evolution suggests that the superposition state, achieved by manipulating the nuclear spin wavefunctions, is influenced by both the frequency and duration of the microwave pulses. By meticulously controlling the microwave pulse duration, an equal-probability superposition state can be realized at specific durations, facilitating the construction of a Hadamard gate. Figure 8b illustrates the probability evolution curves for two nuclear spin states, | + 3/2 and | + 1/2, under different MW pulse durations when the initial nuclear spin state is $| + 1/2 \rangle$. It can be observed from the figure that when the frequency of the MW pulse is 3.1 MHz and the pulse duration is 115 ns, the two states have the same probability of occurrence. Similarly, as the nuclear spin state is increased to three or four levels, the Hadamard gate can be concurrently constructed using microwave pulses with distinct resonance frequencies and pulse widths, as depicted in Figure 8c,d. This capability signifies that the coherent superposition of nuclear spin states can be induced with flexibility and selectivity.

The subsequent phase of the Grover algorithm is targeted at amplifying the target state, which means evolving the system again through coherent manipulations so that the target state occurs with a maximum probability. By establishing a resonance condition between the equal-probability superposition state and the target state, the system is induced to oscillate between these states before evolving definitively toward the target state under certain conditions. This oscillation can be achieved by applying a second microwave pulse. In Figure 8e-g, under the equalprobability superposition state of three nuclear spins, the MW pulses with frequencies of 3.4, 3.0, and 3.9 MHz are applied again, respectively, instigating oscillations in the nuclear spin states of $|-3/2\rangle$, $|-1/2\rangle$, and $|+1/2\rangle$, and the superposition state. As the duration of the microwave pulse increases, the probability distribution of the final system will gradually converge toward the target nuclear spin state, realizing the search for the target state. Anchored in the nuclear spin qubits of SMMs and the refined Grover algorithm, this research has, for the first time, successfully implemented quantum computing at the nanoscale. This pioneering accomplishment bears profound scientific significance, propelling the exploration and development of single-molecule quantum computing technology into uncharted territories.

SCIENCE NEWS _____ www.advancedsciencenews.com small methods www.small-methods.com



Figure 8. Implementation of quantum algorithm. a) Energy levels of four nuclear spin states. b–d) Evolution of the population of nuclear spin state as a function of the duration time τ of MW pulse. e–g) Oscillations between three superposition nuclear spin states and the target state through the MW pulse. Reproduced with permission.^[101] Copyright 2017, American Physical Society.

4. Conclusion and Prospect

Molecular spintronics is a vanguard field at the confluence of molecular electronics and the pioneering principles of spintronics. This synergy is strategically harnessed through magnetic metal complexes, with metal complexes assuming a central role. These spin systems, with their distinctive attributes, provide an optimal arena for scrutinizing spin effects at the single-molecule level. Moreover, devices centered on metal complexes offer exceptional vantages for probing spin dynamics at the molecular scale. Further, meticulous investigations into the nuclear spin of metal complexes yield a holistic portrait of spin characteristics, enabling a spectrum of practical applications.

In this review, we delve into the realm of electron and nuclear spins in metal complexes with a single goal: to unravel the mysteries surrounding their nanoscale properties. The fundamental quantum physics of spin and the intricate processes that govern its manipulation have come into focus. Meanwhile, we also emphasize the innovative approaches for the meticulous management of spin quantum information.

Despite the considerable progress in understanding the spinrelated facets of metal complexes, it remains a need for further investigation into several key issues. 1) How to achieve spin polarization in metal complexes? The ability to electrically control spin transport at the single-molecule level is highly desired in the realm of molecular spintronics. Nevertheless, achieving efficient control over the direction of spin polarization remains a challenge. Therefore, it is essential to investigate effective approaches for realizing practical and reliable spin polarization. 2) How to read out single-molecule spin signals? Transport electrons inevitably interact with the spin state of a single molecule, leading to significant quantum decoherence. This brings substantial difficulties and challenges in reading the spin state of a single molecule. Thus, it is worthy to explore different strategies for precise detection of molecular spin states. 3) What is the relationship between molecular spin and chirality? The chiral-induced spin selectivity (CISS) effect establishes a direct link between the chirality of molecules and their spin states, opening possibilities for spin-based molecular devices. Moreover, achieving chiral selectivity in chemical reactions based on electron spin polarization of molecules has become one of the important research goals in chemistry and biochemistry. 4) How does the spin state of metal complex catalysts regulate the activity and selectivity of reactions? The spin state of metal complex catalysts plays a crucial role in the selectivity and activity of reactions. However, the current understanding of molecular spins in catalytic reactions is rather limited. It could influence reaction pathways and activation energy, and could also achieve selective reaction outcomes, making the tunable spin state of metal complexes a valuable approach in catalytic design. In addition, expectations for the advancement and application of cutting-edge micro-nano fabrication techniques to create integrated metal complex devices are on the rise. This aims to address the issues related to device stability and reproducibility and also promises to broaden the horizons of metal complexes applications in the rapidly expanding domain of quantum information technology, including quantum computing and information processing.



Looking to the future, the research on single-molecule spin qubit device based on metal complexes has broad prospects. The advent of single-molecule spin qubit technology requires innovations that can maximize the potential of metal complexes. As we delve deeper into the single-molecule spin qubit landscape, metal complexes play a critical role in the development of spin qubits with extended coherence times, thus facilitating more robust frameworks for quantum computing. The intersection of metal complexes-based single-molecule spin qubit device with emerging fields such as machine learning may pave the way for transforming our engagement with material science and information technology. The journey to unlocking the complete potential of metal complexes-based single-molecule spin qubit device is fraught with scientific and engineering challenges. The coming decade is anticipated to witness a surge in interdisciplinary research aimed at unraveling the quantum behaviors of metal complexes based on single-molecule spin qubit device and translating these insights into revolutionary technologies. In essence, the fusion of molecular spin qubits with quantum technologies marks a frontier of possibilities. As we stand on the brink of this new era, the pursuit of knowledge and innovation in metal complexes-based single-molecule spin qubit research is accelerating, signaling a future where single-molecule science will redefine the frontiers of computation, communication, and sensing.

Acknowledgements

J.G. and Q.G. contributed equally to this work. The authors acknowledge primary financial support from the National Key R&D Program of China (2021YFA1200102, 2021YFA1200101, and 2022YFE0128700), the National Natural Science Foundation of China (22173050, 22150013, 21727806, and 21933001), the Beijing National Laboratory for Molecular Sciences (BNLMS-CXXM-202407) and the Natural Science Foundation of Beijing (2222009).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

molecular spintronics, nuclear spin manipulation, single-molecule magnet, spin crossover, spin effect

Received: August 18, 2024 Revised: October 28, 2024 Published online:

- S. H. Yang, R. Naaman, Y. Paltiel, S. S. P. Parkin, Nat. Rev. Phys. 2021, 3, 328.
- [2] M. R. Wasielewski, M. D. E. Forbes, N. L. Frank, K. Kowalski, G. D. Scholes, J. Yuen-Zhou, M. A. Baldo, D. E. Freedman, R. H. Goldsmith, T. Goodson, M. L. Kirk, J. K. McCusker, J. P. Ogilvie, D. A. Shultz, S. Stoll, K. B. Whaley, *Nat. Rev. Chem.* **2020**, *4*, 490.
- [3] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnár, M. L. Roukes, A. Y. Chtchelkanova, D. M. Treger, *Science* 2001, 294, 1488.

- [4] J. Grollier, D. Querlioz, K. Y. Camsari, K. Everschor-Sitte, S. Fukami, M. D. Stiles, Nat. Electron. 2020, 3, 360.
- [5] Z. Huang, Y. Zhang, H. Yang, H. Song, Y. Cen, W. Kai, Chem. Soc. Rev. 2017, 46, 1955.
- [6] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, D. M. Treger, *Science* 2001, 294, 1488.
- [7] L. Bogani, W. Wernsdorfer, *Nat. Mater.* **2008**, *7*, 179.
- [8] X. Y. Gao, S. Vaidya, K. J. Li, P. Ju, B. Y. Jiang, Z. J. Xu, A. E. L. Allcca, K.
 H. Shen, T. Taniguchi, K. Watanabe, S. A. Bhave, Y. P. Chen, Y. Ping,
 T. C. Li, *Nat. Mater.* 2022, *21*, 1024.
- [9] J. J. Pla, K. Y. Tan, J. P. Dehollain, W. H. Lim, J. J. L. Morton, F. A. Zwanenburg, D. N. Jamieson, A. S. Dzurak, A. Morello, *Nature* 2013, 496, 334.
- [10] M. V. G. Dutt, L. Childress, L. Jiang, E. Togan, J. Maze, F. Jelezko, A. S. Zibrov, P. R. Hemmer, M. D. Lukin, *Science* 2007, 316, 1312.
- [11] E. Burzurí, R. Gaudenzi, H. S. J. van der Zant, J. Phys. Condens. Matter 2015, 27, 113202.
- [12] G. Christou, D. Gatteschi, D. N. Hendrickson, R. J. M. B. Sessoli, MRS Bull. 2000, 25, 66.
- [13] G. Cosquer, Y. B. Shen, M. Almeida, M. Yamashita, *Dalton Trans.* 2018, 47, 7616.
- [14] L. Sun, Y. A. Diaz-Fernandez, T. A. Gschneidtner, F. Westerlund, S. Lara-Avila, K. Moth-Poulsen, *Chem. Soc. Rev.* 2014, 43, 7378.
- [15] J. Hao, B. Wang, C. Zhao, Y. Huo, J. Wang, C. Jia, X. Guo, Sci. China Mater. 2024, 67, 1994.
- [16] M. Reed, C. J. Zhou, *Science* **1997**, *278*, 252.
- [17] H. Park, A. K. L. Lim, A. P. Alivisatos, J. Park, P. L. McEuen, Appl. Phys. Lett. **1999**, 75, 301.
- [18] B. Q. Xu, N. J. J. Tao, Science 2003, 301, 1221.
- [19] Y. Cao, S. H. Dong, S. Liu, L. He, L. Gan, X. M. Yu, M. L. Steigerwald, X. S. Wu, Z. F. Liu, X. F. Guo, Angew. Chem., Int. Ed. 2012, 51, 12228.
- [20] A. A. Khajetoorians, J. Wiebe, B. Chilian, R. Wiesendanger, Science 2011, 332, 1062.
- [21] G. Ke, C. Duan, F. Huang, X. Guo, InfoMat 2020, 2, 92.
- [22] B. Bederson, Phys. Rev. Lett. 2008, 101, 010002.
- [23] A. C. Aragonès, D. Aravena, F. J. Valverde-Muñoz, J. A. Real, F. Sanz,
 I. Díez-Pérez, E. Ruiz, J. Am. Chem. Soc. 2017, 139, 5768.
- [24] J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruña, P. L. McEuen, D. C. Ralph, *Nature* 2002, 417, 722.
- [25] K. Ono, D. G. Austing, Y. Tokura, S. Tarucha, *Science* **2002**, *297*, 1313.
- [26] J. de Bruijckere, P. Gehring, M. Palacios-Corella, M. Clemente-León, E. Coronado, J. Paaske, P. Hedegård, H. S. J. van der Zant, *Phys. Rev. Lett.* 2019, *122*, 197701.
- [27] W. Haas, J. D. Boer, G. J. Berg, Physica 1934, 1, 1115.
- [28] J. Kondo, Prog. Theor. Phys. 1964, 32, 37.
- [29] G. D. Scott, D. Natelson, ACS Nano 2010, 4, 3560.
- [30] J. J. Parks, A. R. Champagne, T. A. Costi, W. W. Shum, A. N. Pasupathy, E. Neuscamman, S. Flores-Torres, P. S. Cornaglia, A. A. Aligia, C. A. Balseiro, G. K. L. Chan, H. D. Abruña, D. C. Ralph, *Science* **2010**, *328*, 1370.
- [31] H. Fu, X. Zhu, P. Li, M. Li, L. Yang, C. Jia, X. Guo, J. Mater. Chem. C 2022, 10, 2375.
- [32] P. W. Anderson, Phys. Rev. 1961, 124, 41.
- [33] X. Xie, P. Li, Y. Xu, L. Zhou, Y. Yan, L. Xie, C. Jia, X. Guo, ACS Nano 2022, 16, 3476.
- [34] D. Goldhaber-Gordon, J. Göres, M. A. Kastner, H. Shtrikman, D. Mahalu, U. Meirav, Phys. Rev. Lett. 1998, 81, 5225.
- [35] A. D. Zhao, Q. X. Li, L. Chen, H. J. Xiang, W. H. Wang, S. Pan, B. Wang, X. D. Xiao, J. L. Yang, J. G. Hou, Q. S. Zhu, *Science* **2005**, *309*, 1542.
- [36] W. J. Liang, M. P. Shores, M. Bockrath, J. R. Long, H. Park, *Nature* 2002, 417, 725.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

- [37] M. N. Leuenberger, D. Loss, *Nature* **2001**, *410*, 789.
- [38] N. Ishikawa, M. Sugita, W. Wernsdorfer, Angew. Chem., Int. Ed. 2005, 44, 2931.
- [39] R. Vincent, S. Klyatskaya, M. Ruben, W. Wernsdorfer, F. Balestro, *Nature* 2012, 488, 357.
- [40] P. Zhao, Q. H. Wu, D. S. Liu, G. Chen, J. Chem. Phys. 2014, 140, 044311.
- [41] S. Sanvito, Nat. Phys. 2010, 6, 562.
- [42] F. R. Renani, G. Kirczenow, Phys. Rev. B 2013, 87, 121403.
- [43] M. Urdampilleta, S. Klyatskaya, J. P. Cleuziou, M. Ruben, W. Wernsdorfer, Nat. Mater. 2011, 10, 502.
- [44] A. C. Aragonès, D. Aravena, J. I. Cerdá, Z. Acís-Castillo, H. P. Li, J. A. Real, F. Sanz, J. Hihath, E. Ruiz, I. Díez-Pérez, *Nano Lett.* **2016**, *16*, 218.
- [45] K. Yang, H. Chen, T. Pope, Y. Hu, L. Liu, D. Wang, L. Tao, W. Xiao, X. Fei, Y.-Y. Zhang, H.-G. Luo, S. Du, T. Xiang, W. A. Hofer, H.-J. Gao, *Nat. Commun.* 2019, 10, 3599.
- [46] S. Koley, S. Chakrabarti, J. Phys. Chem. C 2017, 121, 21695.
- [47] G. M. Espallargas, E. Coronado, *Chem. Soc. Rev.* **2018**, *47*, 533.
- [48] L. Kipgen, M. Bernien, F. Tuczek, W. Kuch, Adv. Mater. 2021, 33, 2008141.
- [49] M. Gruber, R. Berndt, Magnetochemistry 2020, 6, 35.
- [50] P. Li, L. Zhou, C. Zhao, H. Ju, Q. Gao, W. Si, L. Cheng, J. Hao, M. Li, Y. Chen, C. Jia, X. Guo, *Rep. Prog. Phys.* **2022**, *85*, 086401.
- [51] G. Kuang, Q. Zhang, T. Lin, R. Pang, X. Shi, H. Xu, N. Lin, ACS Nano 2017, 11, 6295.
- [52] E. A. Osorio, K. Moth-Poulsen, H. S. J. van der Zant, J. Paaske, P. Hedegard, K. Flensberg, J. Bendix, T. Bjornholm, *Nano Lett.* 2010, 10, 105.
- [53] H. Hao, X. H. Zheng, L. L. Song, R. N. Wang, Z. Zeng, Phy. Rev. Lett. 2012, 108, 017202.
- [54] M. Gruber, V. Davesne, M. Bowen, S. Boukari, E. Beaurepaire, W. Wulfhekel, T. Miyamachi, Phy. Rev. B 2014, 89, 195415.
- [55] G. D. Harzmann, R. Frisenda, H. S. J. van der Zant, M. Mayor, Angew. Chem., Int. Ed. 2015, 54, 13425.
- [56] S. Wagner, F. Kisslinger, S. Ballmann, F. Schramm, R. Chandrasekar, T. Bodenstein, O. Fuhr, D. Secker, K. Fink, M. Ruben, H. B. Weber, *Nat. Nanotechnol.* 2013, *8*, 575.
- [57] M. Feng, Z.-Y. Ruan, Y.-C. Chen, M.-L. Tong, Chem. Com. 2020, 56, 13702.
- [58] C. Waeckerlin, D. Chylarecka, A. Kleibert, K. Mueller, C. Iacovita, F. Nolting, T. A. Jung, N. Ballav, *Nat. Commun.* 2010, 1, 61.
- [59] G. Neyens, Rep. Prog. Phys. 2003, 66, 633.
- [60] A. Schneider, B. Sikora, S. Dickopf, M. Müller, N. S. Oreshkina, A. Rischka, I. A. Valuev, S. Ulmer, J. Walz, Z. Harman, C. H. Keitel, A. Mooser, K. Blaum, *Nature* 2022, 606, 878.
- [61] W. Liu, M. G. Boshier, S. Dhawan, O. van Dyck, P. Egan, X. Fei, M. G. Perdekamp, V. W. Hughes, M. Janousch, K. Jungmann, D. Kawall, F. G. Mariam, C. Pillai, R. Prigl, G. zu Putlitz, I. Reinhard, W. Schwarz, P. A. Thompson, K. A. Woodle, *Phys. Rev. Lett.* **1999**, *82*, 711.
- [62] A. Nikiel, P. Blümler, W. Heil, M. Hehn, S. Karpuk, A. Maul, E. Otten, L. M. Schreiber, M. Terekhov, *Eur. Phys. J. D* 2014, 68, 330.
- [63] M. Farooq, T. Chupp, J. Grange, A. Tewsley-Booth, D. Flay, D. Kawall, N. Sachdeva, P. Winter, *Phys. Rev. Lett.* **2020**, *124*, 223001.
- [64] H. Schuessler, E. Fortson, H. Dehmelt, Phys. Rev. X 1969, 187, 5.
- [65] L. Zaporski, N. Shofer, J. H. Bodey, S. Manna, G. Gillard, M. H. Appel, C. Schimpf, S. F. C. da Silva, J. Jarman, G. Delamare, G. Park, U. Haeusler, E. A. Chekhovich, A. Rastelli, D. A. Gangloff, M. Atatüre, C. L.e Gall, *Nat. Nanotechnol.* **2023**, *18*, 257.
- [66] A. C. Zemach, Phys. Rev. 1956, 104, 1771.
- [67] S. Shehada, M. dos Santos Dias, F. S. M. Guimaraes, M. Abusaa, S. Lounis, NPJ Comput. Mater. 2021, 7, 87.
- [68] P. Willke, Y. Bae, K. Yang, J. L. Lado, A. Ferrón, T. Choi, A. Ardavan, J. Fernández-Rossier, A. J. Heinrich, C. P. Lutz, *Science* 2018, *362*, 336.

- [69] E. D. Hedegård, J. Kongsted, S. P. A. Sauer, J. Chem. Theory Comput. 2013, 9, 2380.
- [70] Y. S. Ding, K. X. Yu, D. Reta, F. Ortu, R. E. P. Winpenny, Y. Z. Zheng, N. F. Chilton, *Nat. Commun.* **2018**, *9*, 313467.
- [71] R. Wild, M. Nötzold, M. Simpson, T. D. Tran, R. Wester, *Nature* 2023, 615, 425.
- [72] R. J. McMahon, Science 2003, 299, 833.
- [73] M. Mannini, F. Pineider, C. Danieli, F. Totti, L. Sorace, P. Sainctavit, M. A. Arrio, E. Otero, L. Joly, J. C. Cezar, A. Cornia, R. Sessoli, *Nature* 2010, 468, 417.
- [74] L. Thomas, F. R. Lionti, R. Ballou, D. Gatteschi, B. J. N. Barbara, *Nature* **1996**, *383*, 145.
- [75] J. R. Friedman, M. P. Sarachik, J. Tejada, R. Ziolo, Phys. Rev. Lett. 1996, 76, 3830.
- [76] M. Uehara, B. Barbara, B. Dieny, P. C. Stamp, *Phys. Lett. A* **1986**, *114*, 23.
- [77] M. Urdampilleta, S. Klyatskaya, M. Ruben, W. Wernsdorfer, *Phy. Rev. B* 2013, *87*, 195412.
- [78] S. Thiele, R. Vincent, M. Holzmann, S. Klyatskaya, M. Ruben, F. Balestro, W. Wernsdorfer, *Phys. Rev. Lett.* 2013, 111, 037203.
- [79] A. Einstein, W. J. Haas, KNAW 1915, 18, 696.
- [80] M. Ganzhorn, S. Klyatskaya, M. Ruben, W. Wernsdorfer, Nat. Commun. 2016, 7, 11443.
- [81] M. Ganzhorn, S. Klyatskaya, M. Ruben, W. Wernsdorfer, Nat. Nanotechnol. 2013, 8, 165.
- [82] M. Urdampilleta, S. Klyatskaya, M. Ruben, W. Wernsdorfer, *Phys. Rev. B* 2013, *87*, 195412.
- [83] M. P. Williamson, T. F. Havel, K. Wüthrich, J. Mol. Biol. 1985, 182, 295.
- [84] P. C. Maurer, G. Kucsko, C. Latta, L. Jiang, N. Y. Yao, S. D. Bennett, F. Pastawski, D. Hunger, N. Chisholm, M. Markham, D. J. Twitchen, J. I. Cirac, M. D. Lukin, *Science* **2012**, *336*, 1283.
- [85] C. Godfrin, S. Thiele, A. Ferhat, S. Klyatskaya, M. Ruben, W. Wernsdorfer, F. Balestro, ACS Nano 2017, 11, 3984.
- [86] M. R. Yun, F. Q. Guo, L. L. Yan, E. Liang, Y. Zhang, S. L. Su, C. X. Shan, Y. Jia, *Phy. Rev. A* **2022**, *105*, 012611.
- [87] J. M. Taylor, P. Cappellaro, L. Childress, L. Jiang, D. Budker, P. R. Hemmer, A. Yacoby, R. Walsworth, M. D. Lukin, *Nat. Phys.* 2008, 4, 810.
- [88] M. Ruf, N. H. Wan, H. Choi, D. Englund, R. Hanson, J. Appl. Phys. 2021, 130, 070901.
- [89] M. Steger, K. Saeedi, M. L. W. Thewalt, J. J. L. Morton, H. Riemann, N. V. Abrosimov, P. Becker, H. J. Pohl, *Science* 2012, *336*, 1280.
- [90] E. Moreno-Pineda, C. Godfrin, F. Balestro, W. Wernsdorfer, M. Ruben, Chem. Soc. Rev. 2018, 47, 501.
- [91] S. Thiele, F. Balestro, R. Ballou, S. Klyatskaya, M. Ruben, W. Wernsdorfer, *Science* 2014, 344, 1135.
- [92] A. Gaita-Ariño, F. Luis, S. Hill, E. Coronado, Nat. Chem. 2019, 11, 301.
- [93] H. S. Zhong, H. Wang, Y. H. Deng, M. C. Chen, L. C. Peng, Y. H. Luo, J. Qin, D. Wu, X. Ding, Y. Hu, P. Hu, X. Y. Yang, W. J. Zhang, H. Li, Y. X. Li, X. Jiang, L. Gan, G. W. Yang, L. X. You, Z. Wang, L. Li, N. L. Liu, C. Y. Lu, J. W. Pan, *Science* **2020**, *370*, 1460.
- [94] H. Liu, K. Wang, F. Gao, J. Leng, Y. Liu, Y. C. Zhou, G. Cao, T. Wang, J. J. Zhang, P. H. Huang, H. O. Li, G. P. Guo, *Nano Lett.* **2023**, *23*, 3810.
- [95] J. J. Qin, B. Sun, G. D. Zhou, T. Guo, Y. Z. Chen, C. Ke, S. S. Mao, X. L. Chen, J. Y. Shao, Y. Zhao, ACS Mater. Lett. 2023, 5, 2197.
- [96] P. Kwiat, K. Mattle, H. Weinfurter, A. Zeilinger, A. Sergienko, Y. H. Shih, Phys. Rev. Lett. 1995, 75, 4337.
- [97] C. Y. Lu, D. E. Browne, T. Yang, J. W. Pan, Phys. Rev. Lett. 2007, 99, 250505.

SMO

www.small-methods.com



small methods www.small-methods.com

- [98] B. P. Lanyon, T. J. Weinhold, N. K. Langford, M. Barbieri, D. F. V. James, A. Gilchrist, A. G. White, *Phys. Rev. Lett.* **2007**, *99*, 250505.
- [99] A. Politi, J. C. F. Matthews, J. L. O' Brien, Science 2009, 325, 1221.
- [100] L. K. Grover, Phys. Rev. Lett. 1997, 79, 325.
- [101] C. Godfrin, A. Ferhat, R. Ballou, S. Klyatskaya, M. Ruben, W. Wernsdorfer, F. Balestro, Phys. Rev. Lett. 2017, 119, 187702.



Jie Guo received her Ph.D. degree in 2020 from the Institute of Chemistry, Chinese Academy of Sciences. She is currently engaged in postdoctoral research with Prof. Xuefeng Guo and Prof. Chuancheng Jia at the College of Electronic Information and Optical Engineering, Nankai University. Her current research is focused on precision fabrication technology for single-molecule devices.



Qinghua Gao received his M.S. degree in 2021 from Jilin University. He is currently a Ph.D. candidate at the College of Electronic Information and Optical Engineering, Nankai University, under the supervision of Prof. Xuefeng Guo and Prof. Chuancheng Jia. His research is focused on single-molecule electronics.



Fei Gao received her Ph.D. degree in 2015 from the Institute of Physics, Chinese Academy of Sciences, Beijing. From 2015, she was a postdoc at the Beijing Computational Science Research Center, Technical University of Denmark, and Donostia International Physics Center. Her research is focused on molecular spintronics.



Chuancheng Jia received his Ph.D. degree in 2014 from the College of Chemistry and Molecular Engineering, Peking University, under the guidance of Prof. Xuefeng Guo. From 2014 to 2020, he was a postdoc at the Institute of Chemistry, Chinese Academy of Sciences, and University of California, Los Angeles. He joined the faculty as a professor at Nankai University in 2020. His research is focused on single-molecule electronics and dynamics.





Xuefeng Guo received his B.S. degree in 1998 from Beijing Normal University and his Ph.D. degree in 2004 from the Institute of Chemistry, Chinese Academy of Sciences, Beijing. From 2004 to 2007, he was a postdoc at the Columbia University Nanocenter. He joined the faculty as a professor under the "Peking 100-Talent" Program at Peking University in 2008. His current research is focused on single-molecule science and technology.