

Exploiting chemistry and molecular systems for quantum information science

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Abstract | The power of chemistry to prepare new molecules and materials has driven the quest for new approaches to solve problems having global societal impact, such as in renewable energy, healthcare and information science. In the latter case, the intrinsic quantum nature of the electronic, nuclear and spin degrees of freedom in molecules offers intriguing new possibilities to advance the emerging field of quantum information science. In this Perspective, which resulted from discussions by the co-authors at a US Department of Energy workshop held in November 2018, we discuss how chemical systems and reactions can impact quantum computing, communication and sensing. Hierarchical molecular design and synthesis, from small molecules to supramolecular assemblies, combined with new spectroscopic probes of quantum coherence and theoretical modelling of complex systems, offer a broad range of possibilities to realize practical quantum information science applications.

Chemistry is fundamental to the development of complex matter that can address critical societal problems ranging from energy production to healthcare and information sciences. Similarly, molecular design and synthesis are now being applied to the rapidly expanding field of quantum information science (QIS). QIS seeks to harness the fundamental quantum nature of matter and energy to greatly advance computation, communication and sensing. In turn, the development of QIS applications, especially in terms of computing and networking, will greatly impact the development of methods to design new molecules and materials, thus, providing strong, positive feedback for new chemical applications. A brief description of QIS is given in BOX 1.

As chemists enter the QIS field, a question to consider is what quantum resources present opportunities for discovery in chemistry. The variety of

concepts chemists need to translate from theories, often abstract, to molecular systems and experiments include those listed in BOX 2. Chemists are generally familiar with quantum bits (qubits) and the concept of quantum coherence, and are well versed in preparing specific molecular quantum states. However, the discovery and characterization of complex molecular systems for QIS that exploit a variety of quantum resources will require fulfilling additional challenging criteria, but will also provide opportunities for the coming decade.

In 2000, DiVincenzo enumerated a set of now well-known criteria for quantum computing, quantum communication and sensing, which has provided a useful foundation for molecular-qubit design principles¹. Desirable molecular characteristics specific to quantum computing include: (1) the ability to initialize a qubit in a well-defined quantum state. For example, this often means

preparing a typical two-state system so that all the population is in one of the two states. (2) The qubit must exhibit long coherence times, although systems with shorter coherence times may also be of interest (as we discuss below). Electronic coherences most often decay in less than 1 ps, vibronic and vibrational coherences last several ps, whereas electron and nuclear spin coherences are much longer-lived, extending to μ s–ms and ms–s, respectively. Tailoring molecular structures and their surrounding environment to maximize coherence times is currently a major challenge. (3) The system must provide a set of universal quantum logic gates that operate on one or two entangled molecular qubits². Quantum gates can be generated by physical and chemical perturbations of the system, such as applied fields and chemical reactions. (4) The outcomes of a qubit should be measured in a specific manner, following their unique spectroscopic signatures. As we will discuss below, these measurements are frequently performed using time-resolved spectroscopies. Additional characteristics are required for qubits used in quantum communications and/or sensing. Both stationary and flying (moveable) qubits used for computation and sensing, and in communications protocols, respectively, should be easy to produce and control. Furthermore, a faithful transmission of these flying qubits between specific sites needs to be assured. Photons are most often employed as moveable qubits, so that our photophysical and photochemical knowledge of molecular systems can be exploited in this regard. From a chemistry perspective, ease of synthesis, ability to prepare complex architectures, scalability and low cost should be added to the above criteria.

Current materials used in quantum computing are designed to increase the coherence times of single qubits by isolating them from their environment, while providing them properties that enable their individual measurement and information readout. For example, a leading contender for near-term quantum-computing technology is the superconducting qubit based on the Josephson effect³. Progress on this approach was greatly accelerated by the development of a particular type

of superconducting charge qubit — the transmon qubit⁴ — that is designed to greatly reduce quantum noise causing the loss of coherence. These systems have been

scaled to the tens of qubits level but require mK temperatures to overcome residual noise. Laser-cooled trapped ions is another well-established qubit implementation that

has also been scaled to the tens of qubits level. Quantum logic gates using trapped-ion spin states have been demonstrated^{5,6} but require ultrahigh vacuum conditions, along with cryogenic cooling to minimize noise in ever-smaller ion-trap configurations. Similar experimental advantages and constraints appear in manipulating neutral atoms for QIS applications⁷. III–V and group IV semiconductor quantum dots have also been fabricated^{8,9}. For example, silicon quantum dots take advantage of state-of-the-art, scalable, industrial nanofabrication capabilities and offer some of the longest quantum coherence times measured in the solid state^{8,9}. Once again, low temperatures are commonly necessary and isotopes with no nuclear spin are used to magnetically isolate single or small ensembles of electron spins in quantum dots to achieve long coherence times.

Qubits based on defects such as nitrogen vacancy (NV⁻) centres in diamond or single-vacancy or divacancy centres in SiC hold great promise because of the wide temperature range over which they can maintain spin coherence¹⁰. Although the longest spin coherence times can still only be achieved at mK temperatures, some applications, such as quantum sensing, can take advantage of the more modest coherence times observed at higher temperatures. Furthermore, the highly pure initial spin quantum state for NV⁻ centres in diamond can be obtained using visible photons and manipulated using microwave photons. The result of these operations can then be read out using fluorescence emission from the defect centre, which means that optically detected magnetic resonance techniques can be used to address single defect sites^{10,11}. Currently, the main drawback of qubits based on defect centres is the difficulty in fabricating them at specific locations and selectively addressing different centres.

In striking contrast to the approaches described above, chemical synthesis affords the opportunity to build new QIS systems from the bottom up, taking full advantage of the quantum properties of matter on the atomic length scale. Atomic-level control over both the quantum states that define the qubits, as well as the interaction between qubits that define the superposition and entanglement of their states, are critical to advancing QIS. Several recent review articles have focused on different chemical approaches to qubits, such as paramagnetic metal complexes with controlled ligand environments^{12–16}, single-ion magnets based on lanthanides and actinides¹⁷, and molecules that can employ more than

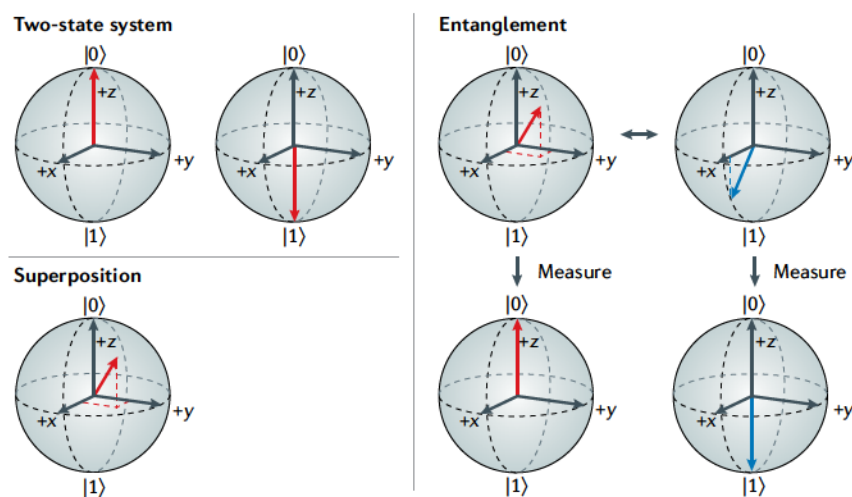
Box 1 | Fundamentals of QIS

Quantum information science (QIS) exploits the intrinsic quantum nature of matter and photons to develop new approaches to computing, communications and sensing. The two basic quantum properties that QIS takes advantage of are superposition and entanglement of quantum states. The simplest examples of these phenomena involve two-state systems, such as electron spins and photons. For example, if we place an electron spin in a magnetic field, the two relevant quantum states are ‘spin up’ or ‘spin down’, based on the orientation of the magnetic moment of the electron parallel or antiparallel to the field, respectively. An analogous, two-state quantum property of photons is polarization. If we focus on electron spin, observing or measuring the spin will result in spin up $|0\rangle$ or spin down $|1\rangle$ relative to the external magnetic field (see the figure, top-left panel). However, in the absence of a measurement, the electron spin exists in a superposition state (see the figure, bottom-left panel), in which its wave function can be described by $\psi = a|0\rangle + b|1\rangle$, where a and b are two coefficients. If two or more electron spins interact with one another through magnetic exchange or a dipole–dipole interaction, they can become entangled. The idea of entanglement is at the foundational heart of quantum mechanics. The now famous arguments between Bohr and Einstein over the ‘realism’ of quantum-mechanical phenomena that began in 1927 reached a crescendo in 1935 when Einstein, Podolsky and Rosen discussed the issue of how a measurement carried out on one electron spin of an interacting pair affects the other²⁰⁶. A definitive answer to this problem waited until 1964, when John Bell published his paper²⁰⁷, proving that quantum mechanics is intrinsically ‘non-local’, that is, a measurement carried out on one electron would immediately result in the other particle having a definitive result, if it too was subsequently measured, no matter how far away from one another the two particles were (see the figure, right panel). The two-spin system can be described by two-particle wave functions that are the Bell states:

$$\psi_1 = \frac{1}{\sqrt{2}}(|01\rangle - |10\rangle); \psi_2 = \frac{1}{\sqrt{2}}(|01\rangle + |10\rangle); \psi_3 = \frac{1}{\sqrt{2}}(|00\rangle - |11\rangle); \psi_4 = \frac{1}{\sqrt{2}}(|00\rangle + |11\rangle).$$

In general, any molecular property that can be described by a two-particle wave function as illustrated for electron spin can be analysed in terms of Bell states of the quantum system.

These two fundamental ideas are essential to implementing QIS applications. For example, unlike classical computers that rely on bits with only two values, 0 and 1, a quantum computer takes advantage of quantum superposition, making it possible to use any combination of 0 and 1, which, in principle, can greatly increase computational speed. Likewise, if we consider quantum communications, if two sites possess one photon of an entangled photon pair each, information can be transmitted between the two sites by having a third photon interact with one photon of the entangled pair. This strategy, known as quantum teleportation, was first proposed by Bennett²⁰⁸ to overcome the no-cloning theorem of quantum mechanics. Any attempt to eavesdrop on the communication will result in a quantum measurement being made on the entangled photon pair, thus, breaking the entanglement, which indicates that the security of the information transmission has been compromised. In the field of sensing, an electron spin that is in a superposition state is very sensitive to its surrounding environment. Even a weak interaction of an electron spin in a chemical species, such as the influence of a nearby nuclear spin, will elicit a quantum measurement, resulting in sensing of that molecule. The exquisite sensitivity of the superposition state to its surroundings makes it possible to detect single molecules and to even carry out single-molecule magnetic resonance spectroscopy for structural determination.



Schematics are adapted from REF.⁶², Springer Nature Limited.

Box 2 | Key concepts in QIS

- **Quantum resource:** correlations that cannot be described by classical probability laws are deemed a resource in quantum information science (QIS). Most prominent among such correlations are those exhibited by entangled states, and other kinds of quantum resources, such as the coherent superposition of quantum states.
- **Coherence:** refers to a superposition, not necessarily quantum-mechanical, such that the amplitude and phase of the basis states are held 'in step'. Coherence can be obtained by irradiating even very complex systems with short laser pulses or radio-wave/microwave pulses. It can then be controlled or probed by subsequent pulses.
- **Decoherence:** occurs when interactions between the system and environment lead to a loss of coherence between states that were initially superposed. Decoherence can be viewed as a transition from a quantum state that is isolated from the environment to a state that has more classical character as the quantum system mixes with the environmental degrees of freedom.
- **Measurement:** measurement in QIS refers to rigorous characterization of a quantum state, density matrix of an ensemble or detection of a quantum property. This kind of measurement is often indirect and obtained from a comparison to a reference state called a witness.
- **Discord:** quantum discord is an example of a measure that compares quantum subsystems and reveals quantum information that can be more general than entanglement. In this case, non-classical correlations do not need to be specified and, owing to its close connection to classical probability, the measure may be accessible through practical measurements of ensemble quantities.
- **Quantum gate:** similar to a classical logic gate, a quantum logic gate is a quantum circuit that operates on a few qubits. However, unlike many classical logic gates, quantum logic gates are reversible due to the reversible nature of quantum-mechanical operators, i.e. unitary transformations.
- **Quantum noise:** refers to the intrinsic fluctuations of a quantum system that limit the accuracy of measurements.
- **Josephson effect:** refers to lossless current flow in the absence of an applied voltage across a thin insulating barrier placed between two superconductors.

two quantum states¹⁸. The design and synthesis of molecules, nanoparticles, clusters and other zero-dimensional particles into higher-dimensional assemblies enables us to achieve control over the electronic structure of molecular arrays and assemblies at an atomistic level, providing distinct advantages over mesoscopic systems for QIS. The chemically derived species discussed in this Perspective differ from current qubit implementations described above in two important ways. First, chemical synthesis allows control over the nature of the qubit itself, thus, enabling the careful tuning of individual quantum states. Second, covalent and non-covalent interactions between molecules can be used to construct atomically precise arrays of qubits. This approach offers the possibility to interrogate the properties of a qubit in isolation and, subsequently, within an array through molecular design and spectroscopy, providing significant promise for discovering new insights into the quantum properties of multi-qubit arrays.

Applications of molecular systems to QIS

QIS can be explored and applied in a wide range of fields, including computation, communication and sensing. In particular, quantum computation would be useful for the simulation of the electronic structure

and dynamics of realistic molecules and materials, leading to potentially new understandings of catalytic processes, light-harvesting applications and even high-temperature superconductivity, all of which are critical to energy production, storage and electricity transmission¹⁹. QIS holds promise for addressing some insurmountable technological limitations of classical computing, associated with the classical von Neumann processor model, processor frequency, memory and speed of communication. Additionally, QIS modelling tools may be capable of overcoming the exponential scaling of conventional computational approaches for the simulation of chemical transformations that involve multiconfigurational electronic states, which traditionally pose a significant challenge for approximate quantum-chemical methods. However, there are questions that have received much less attention, such as whether quantum communication and sensing have much to offer to chemistry, or, conversely, whether chemistry can provide any new directions for these areas in QIS. In the next few paragraphs, we argue that the latter is, in fact, the case, and that chemistry will have a timely and transformative impact on QIS.

An obvious area of QIS in which chemistry can be advantageous is quantum sensing.

In this case, each qubit can be designed to measure the physical properties of a specific analyte in a system or environment of interest²⁰. For example, the prospect of tuning the spacing between the quantum sensor and the analyte offers transformative potential for sensing small magnetic moments because the spins interact primarily by magnetic dipole coupling that depends on $1/r^3$, where r is the spin–spin distance. Furthermore, molecules can serve as optical qubits that can be initialized through direct generation of excited states, the emission from which can be read by high-sensitivity photodetectors. Quantum sensing is an excellent platform for increasing fundamental understanding across a variety of biosystems, such as viruses, bacteria and neurons. Quantum sensing also refers to the use of non-classical resources such as squeezed or entangled light to obtain enhanced sensitivities in physical measurements²⁰. These resources could be harnessed for the improved detection of analytes, giving rise to new frontiers in analytical chemistry and chemical instrumentation.

A prototypical quantum sensor is an atomic defect in a semiconductor, such as an NV[−] centre in diamond, which features a simple, multilevel optical spectrum that is highly sensitive to changes in electric and magnetic fields, and temperature gradients. Selective excitation and detection of the emission of such NV[−] centres enable the spatially resolved detection of physical property changes in biological^{21–27} and materials systems^{28–30}. However, NV[−] centres are not efficient quantum emitters and have short coherence times, except at very low temperatures^{10,31}. It is reasonable to speculate that small molecules can be optimized to be comparable or better quantum emitters than NV[−] centres, especially for the analysis of biological systems, because of the better biocompatibility of the former³². Furthermore, chemically versatile qubits are likely to be more adept than NV[−] centres to probe the chemical dynamics of single molecules, such as changes in conformation, oxidation state and coordination environment, and, therefore, achieve highly resolved spatio-temporal detection of catalytic processes³³.

Molecules and nanocrystals offer promise as direct means to realize qubits, but also as complements to existing QIS technologies, such as superconducting arrays. The traditional foundation for QIS technologies spans atomic and photonic systems, with more recent developments focusing on atomic defects

in semiconductor crystals³⁴. However, deterministic incorporation of atomic-scale components is challenging within traditional fabrication technologies^{10,31}. Molecules and nanocrystals provide a bridge from atomic to conventional patterning length scales in the sub-10-nm regime, with synthesis offering precise control and reproducibility of molecular structure. Molecules and nanocrystals also exhibit stronger transition dipoles in the ultraviolet (UV)-visible range, which can give rise to improved coupling between molecules and photons, while also providing richer possibilities for engineering transitions between spin sublevels³⁵. Couplings between these quantum emitters and photons are likely to be mediated by optical cavities and, potentially, by the formation of strongly coupled light-matter states or polaritons³⁶. Single-photon non-linearities are possible with single molecules or nanocrystals in small-mode-volume cavities^{37,38}. Perhaps one of the most advanced ways to generate and exploit single-photon emission is based on epitaxial quantum dots positioned within high-quality optical cavities³⁹. To date, however, these devices rely on fortuitous matching between the optical cavity and the quantum emitter within a large inhomogeneous distribution. It will be necessary to develop robust fabrication technologies that precisely position emitters within cavities and enable precise post-fabrication tuning of their optical properties. Successful demonstration of arrays of 'quantum pixels' consisting of precisely tuned molecular or nanocrystal emitters, each exhibiting deterministic production of non-classical states of light (such as single-photon or few-photon states) on demand, could be entangled in linear optics quantum simulators⁴⁰ or harnessed in phased arrays for quantum illumination⁴¹. Furthermore, highly bright quantum photon sources are crucial to increase secure quantum-communication rates. For example, it was shown that the entanglement of two NV⁻ centres was limited to an event rate of approximately 10 Hz by inefficiencies in the single-photon sources⁴².

This Perspective focuses on chemical systems as qubits, with a view towards these new opportunities for the use of chemistry for architectural and structural control of QIS systems, spectroscopy and measurement of molecular systems for QIS, computational methods for designing and understanding molecular systems for QIS and the outlook for exploiting chemistry for QIS applications.

Molecular systems as qubits

The most fundamental feature of a qubit is that it possesses at least two well-defined quantum states, making electron and/or nuclear spins in molecules ideal qubit candidates. A single electron spin qubit may comprise an organic radical or paramagnetic metal centre, in which the number of available spin states is defined by its spin multiplicity ($2S+1$). This ability to go beyond a simple two-state system is an important advantage of molecular systems⁴³. These spin states can be further split by hyperfine interactions, spin-orbit coupling and zero-field splittings. The spin-state population at a given temperature is dictated by Boltzmann statistics, which depends on the energy gap (ΔE) between the spin states and the available thermal energy (kT). Therefore, if $\Delta E \gg kT$, the lowest-energy spin state is fully populated and can be used as a pure quantum state. Several studies have shown how a variety of optical techniques can be used to obtain well-defined electron spin states in molecular systems with desirable QIS properties, including the direct generation of high-multiplicity excited states in organic molecules⁴⁴⁻⁴⁶, photogenerated organic radical pairs and triradicals⁴⁷⁻⁵¹, metal-centred excited states⁵²⁻⁵⁴, metal-centred spin states⁵⁵⁻⁵⁷ and photoisomerization-induced spin-charge excited states⁵⁸. Some representative examples are shown in FIG. 1.

Control of the coherence times of quantum states is currently one of the major challenges in QIS. Spin-state decoherence can be greatly accelerated by interactions such as spin exchange, hyperfine coupling, spin-orbit coupling and magnetic dipolar coupling. By controlling the structure and composition of molecular qubits, many of these decoherence sources can be mitigated and/or controlled^{59,60}. For example, purely organic molecular qubits have the advantages of weak spin-orbit coupling and well-defined electron-electron and electron-nuclear spin-exchange interactions⁴⁷. Moreover, ultrafast photochemical electron transfer within an organic donor-acceptor (D-A) molecule can produce a radical pair that can function as two entangled spin qubits (D^+-A^-), giving rise to an entangled two-spin singlet or triplet state^{59,60}. This strategy has been used to achieve electron spin-state teleportation, which is essential to preserve quantum information across long distances⁶¹, in an ensemble of covalent D-A-R^{*} molecules, in which it is possible to propagate the initially prepared spin state of a stable radical R^{*} to D^+ (REFS^{61,62}). Following preparation of a specific

electron spin state on R^{*} using a microwave pulse to rotate the spin orientation with respect to an external applied magnetic field, photoexcitation of A results in the formation of a singlet entangled electron spin pair D^+-A^- (FIG. 1a,b). The spontaneous ultrafast chemical reaction $D^+-A^--R^* \rightarrow D^+-A^-$ constitutes the Bell state measurement step necessary to achieve spin-state teleportation (BOX 1). Quantum-state tomography of the R^{*} and D^+ spin states using pulse electron paramagnetic resonance (EPR) spectroscopy shows that the spin state of R^{*} is teleported to D^+ with high fidelity. Another study⁵⁴ has shown that excited-state spin wave functions of tripartite systems comprising a stable organic radical ($S = 1/2$) covalently attached to a photogenerated electron-hole pair can be determined explicitly (FIG. 1c). Knowledge of the constituent pairwise exchange parameters allows one to modulate spin entanglement. For example, spin-exchange coupling affects the lifetime of the excited state of the tripartite molecule in a controlled manner by varying the degree to which the relaxation to ground state is spin allowed.

Although specific molecular quantum states can be prepared using the strategies mentioned above, these pure states can be easily perturbed by vibronic coupling, mixing with other energetically accessible states and system-bath coupling, which can make addressing and reading the states difficult. Fortunately, a variety of methods is available that can characterize the nature of magnetic spin exchange (such as EPR⁶³ and optically detected magnetic resonance¹¹ spectroscopies), magnetic susceptibility⁶⁴ and magneto-optic effects⁶⁵ (BOX 3). In addition, molecular qubits can undergo changes in oxidation state⁶⁶, resistivity⁶⁷, electrical gating in transistors⁶⁸ and/or molecular conduction⁶⁹. These measurements can be acquired using radio-frequency scanning tunnelling spectroscopy⁷⁰, spin-polarized scanning tunnelling microscopy⁷¹ and techniques based on the formation of optical cavities and polaritons^{36,72}.

Another underexplored feature of chemically derived systems is the transfer of coherence between electron and nuclear spin qubits, as has been achieved in ³¹P-doped Si in the solid state⁷³. The rapid gate times and high environmental sensitivity of electron spins recommend their application as the operational elements for quantum sensors or logic gates⁷³, whereas the longer coherence times for nuclear spin qubits (10^{-3} – 10^{-4} s)⁷⁴ suggest that they can be best used as storage media^{75,76}. By careful chemical design,

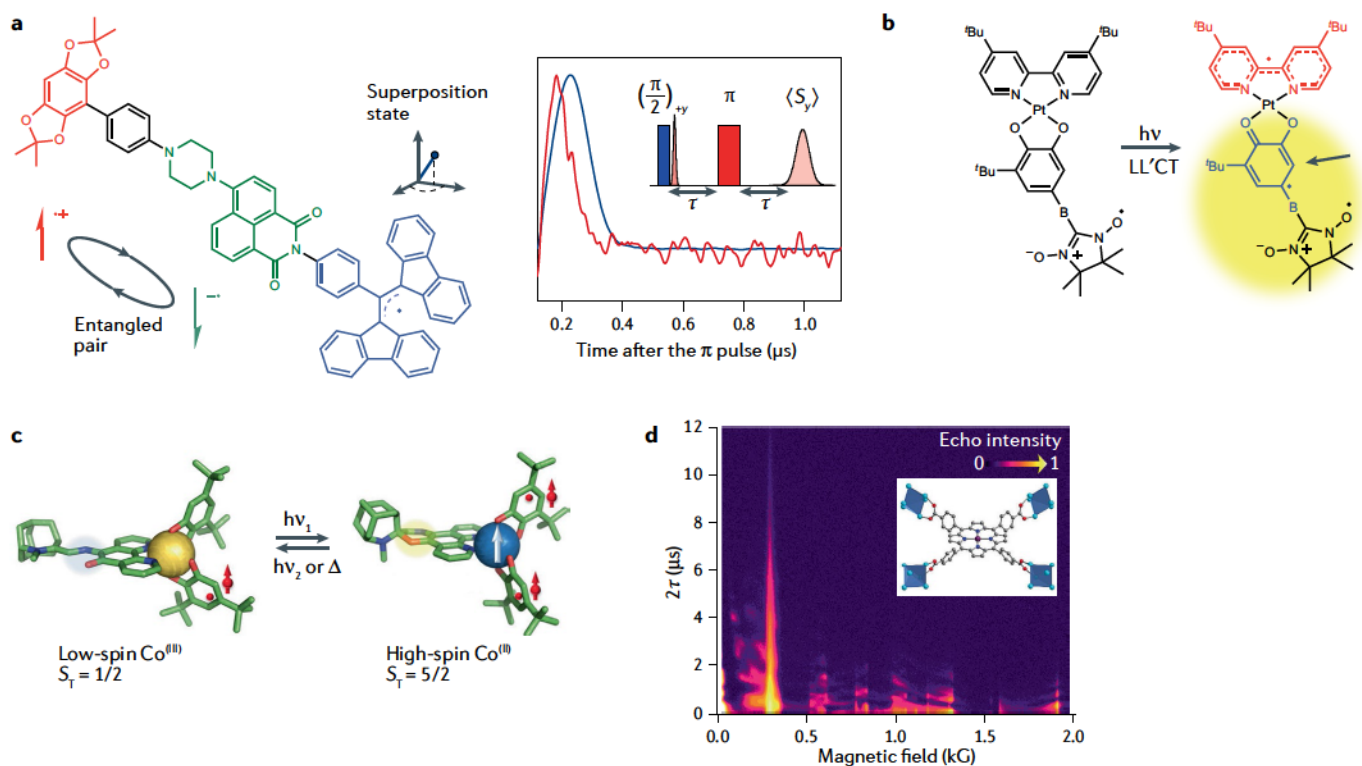


Fig. 1 | Molecular qubit candidates. **a** | Optical control of spin states can be achieved through photogeneration of spin-entangled (magnetic-exchange-coupled) radical pairs in covalent donor-acceptor-radical (D-A-R) systems (left panel) that demonstrate electron spin-state quantum teleportation (right panel)⁶². The blue trace in the graph shows the electron spin echo signal obtained from placing R^* in a coherent spin superposition state using a microwave pulse, whereas the red trace shows the corresponding signal from the teleported state on D^{*+} generated by laser-driven photoreduction of R^* . **b** | Photogeneration of a Pt complex produces spin-entangled radical pairs through strong magnetic exchange in the ligand-to-ligand charge transfer (LL'CT) state of the resulting triradical⁵⁴. The yellow region and accompanying arrow highlight the two organic radicals having entangled spins. **c** | This figure shows a Co complex in which

photoisomerization-induced spin-charge excited-state processes lead to optical modulation of spin states with long decoherence times⁵⁸. The yellow and blue spheres represent $Co^{(II)}$ and $Co^{(I)}$, respectively. **d** | The Coporphyrin in this figure has dramatically elongated spin-spin relaxation times (T_2) as measured by pulse electron paramagnetic resonance spectroscopy using 3.66-GHz microwave pulses at 15 K (REF.⁵⁷). The contour plot shows how T_2 , as indicated by the spin echo intensity, is dramatically longer at a 0.3-kG magnetic field, where the slope of the frequency vs magnetic field dependence for the magnetic transition is zero (a so-called clock transition), rendering the electronic spin insensitive to local fluctuations of the magnetic field. Part **a** is adapted from REF.⁶², Springer Nature Limited. Part **b** is adapted with permission from REF.⁵⁴, ACS. Part **c** is adapted with permission from REF.⁵⁸, ACS. Part **d** is adapted with permission from REF.⁵⁷, RSC.

it is possible to control the distance between electron and nuclear spins, thereby, tuning the rate and efficiency of coherence transfer between them. Indeed, progressing past the current state of the art, it may be possible to create an array of nuclear-spin-based storage units based on $S = 1/2$ nuclei such as ^{19}F , 1H and ^{31}P to harness the unique magnetic properties of each nucleus. Alternatively, in some cases, electron spin systems themselves can be envisioned for quantum-storage memory devices^{77,78}. This is a consequence of recent significant improvements in molecular electron spin coherence times^{56,60}.

Incorporating metals into qubit design confers a range of possible spin states through the choice of both the metal ion and ligand structure with well-understood superexchange and direct-exchange pathways^{79,80}. Coordination complexes^{58,76,81–88} (FIG. 1c) and metal-organic frameworks⁵⁷ (FIG. 1d) featuring transition

metals and lanthanides dramatically expand the synthetic opportunities for qubits and qubit arrays. Stationary two-qubit quantum gates have been proposed in metallic clusters^{66,89} and have been realized in ensembles of molecular magnets^{90,91} and endohedral fullerenes⁹², and even theoretically proposed for superpositions of macroscopically distinct states of molecules (structural or stereoisomers)^{93,94}.

In addition, vibronic interactions in molecular systems can leverage new degrees of freedom. Particularly in transition-metal complexes, a strong degree of coupling can exist between electronic and vibrational degrees of freedom, owing to the large structural perturbations that are often associated with changes in electronic structure from one state to another (for example, ground state versus excited state). Recent evidence suggests a strong dependence of spin-spin relaxation

dynamics (T_2) on the coupling of electronic states to relevant vibrational modes⁹⁵. This coupling can be revealed upon excitation with laser pulses that have sufficient bandwidth (that is, short enough duration) to create excited-state wave packets. It has been shown that the dephasing of these wave packets can help identify which molecular vibrational degrees of freedom are actively engaged in driving vibronic-state evolution⁹⁶. In principle, this information can be fed back into the synthetic design of the compound to modulate coherence times in a design-specific manner. For example, incorporation of a specific vibrational mode into a molecule, such as a $C\equiv C$ or $C\equiv N$ bond, that can be excited using ultrafast infrared laser pulses can induce changes in the reaction coordinate of a chemical process⁹⁷. This control over electronic and nuclear properties cannot be easily realized in solid-state materials, making

molecule-based approaches unique in this regard.

In the previous paragraphs, we argued that molecules offer exciting opportunities to expand the functionalities of qubit architectures. As a concrete example, recently, there has been much interest in ‘polariton chemistry’, the study of ensembles

of molecules in optical cavities^{36,98}.

As opposed to their single-molecule counterpart, dense organic dye layers or microfluidic solutions of highly absorbing molecules can readily undergo collective strong light–matter coupling at room temperature, with the corresponding polaritons inheriting the electromagnetic

coherence of the light modes with which they hybridize. Polaritons have been shown to successfully alter molecular reactivity and optoelectronic characteristics under optical pumping and, remarkably, also under thermal-equilibrium conditions³⁶. Furthermore, non-equilibrium versions of Bose–Einstein condensation of molecular

Box 3 | Experimental techniques commonly used in molecular QIS

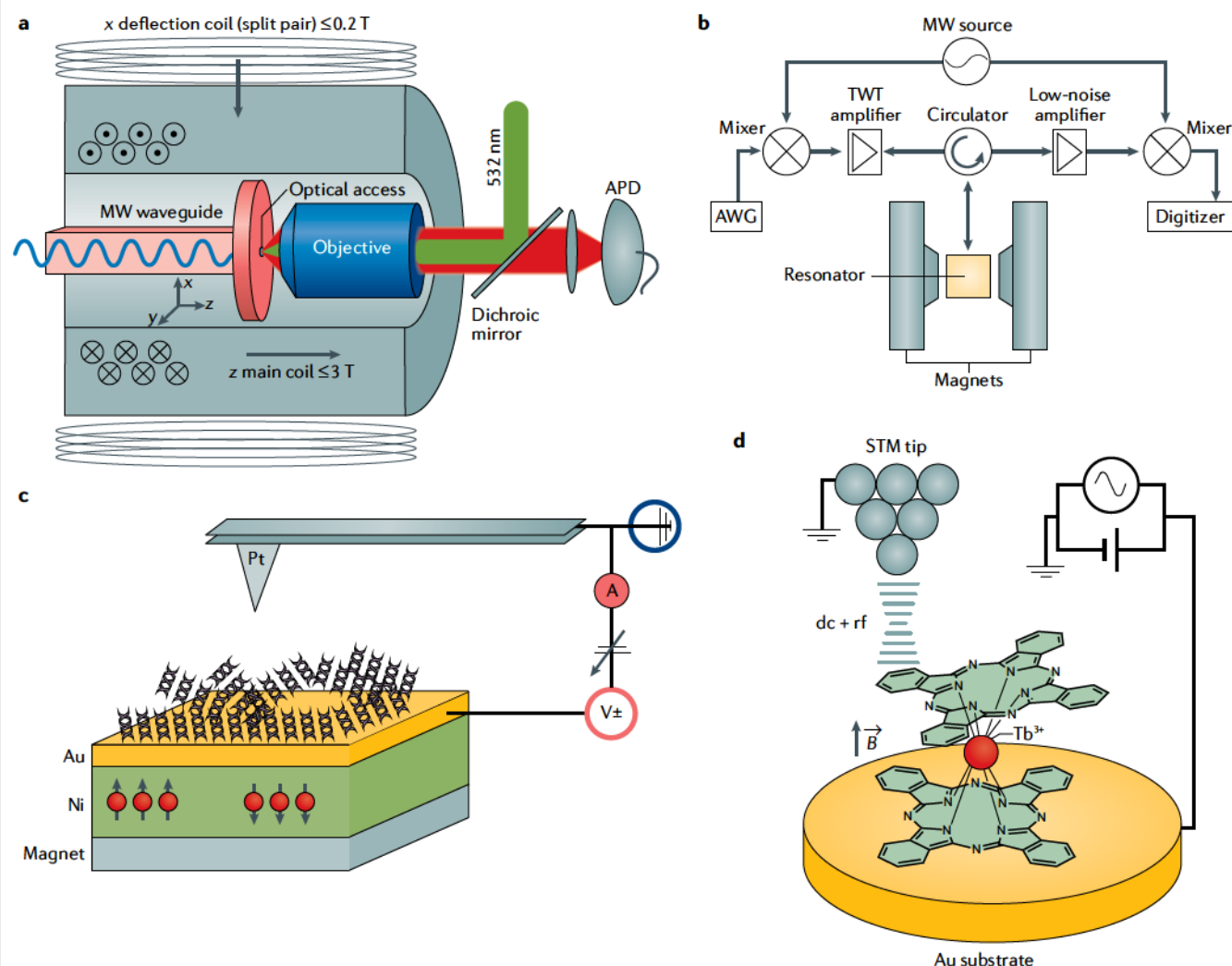
Optically detected magnetic resonance²⁰⁹ (see the figure, panel a). A laser source (532 nm) is used to optically pump a nitrogen vacancy (NV⁻) centre in diamond mounted on a microwave (MW) resonator placed between the poles of a magnet (grey). This pumping spin polarizes the spin sublevels of the triplet ground state of the NV⁻ centre. The spin state of the NV⁻ centre is then read out by observed red-light emission using an avalanche photodiode (APD).

Time-resolved pulse electron paramagnetic resonance spectroscopy⁴⁵. Ensemble measurements in quantum information science (QIS) are performed using pulse electron paramagnetic resonance spectroscopy (see the figure, panel b). The spectrometers have full arbitrary waveform generation capabilities (AWG source) that provide multiple pulse sequences with completely adjustable frequencies, amplitudes, phases and lengths that are amplified with a travelling wave tube (TWT) amplifier.

In typical experiments, optically prepared spin states are manipulated using a sequence of short MW pulses and then read out using MW detection.

Scanning probe microscopy. Scanning probe microscopy is used to perform spin filtering by exploiting oriented chiral molecules deposited on a magnetic substrate¹¹². The figure (panel c) depicts chiral molecules attached to a magnetic Ni substrate being probed by a Pt probe tip. This is a promising technique for generating the highly polarized initial spin states required for QIS applications.

Single-molecule magnetic resonance using scanning tunnelling microscopy (STM). This approach can be used to implement selective addressability of spin states for QIS as shown for the Tb³⁺ complex illustrated (see the figure, panel d) and serves as an analytical tool to determine molecular structures⁷⁰.



Panel a is adapted with permission from REF.²⁰⁹, AIP. Panel c is adapted from REF.¹¹², CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0>). Panel d is adapted with permission from REF.⁷⁰, APS.

polaritons have also been observed in organic chromophores⁹⁹. This emerging field of polariton chemistry borrows concepts from quantum electrodynamics but, in a sense, is a richer enterprise that embraces questions of reactivity, photophysics, charge transport and room-temperature thermodynamics and kinetics. This research direction, thus, inherits the chemical physics tradition of coherent control¹⁰⁰ but marries it into contemporary QIS platforms such as optical microcavities. This union could naturally prompt unique interdisciplinary pursuits. For instance, arrays of molecular polaritons could facilitate the quantum simulation of many-body condensed-matter models¹⁰¹ and, in doing so, possibly also provide unprecedented avenues for controlling molecular processes. For example, strong light–matter interactions can endow molecular matter with unique physico-chemical properties, such as turning transparent materials into strong light absorbers¹⁰². In addition, it may

be possible to remotely control chemistry (FIG. 2) by photoexciting a ‘remote catalyst’ in one cavity to influence the photochemistry of reactant in another cavity using the non-local effect on strong light–matter interactions provided by the cavities¹⁰³.

Chemistry for the design of QIS systems

Chemistry enables the design of large molecular structures with atomic precision. Hierarchical structures known as meta-frameworks, such as metal–organic frameworks, covalent organic frameworks, polymers and crystalline materials, provide a platform for scaling up single-molecule qubits to functional multi-qubit arrays (FIG. 3). Molecular qubits can be connected through linkages that are only a few nanometres long, potentially leading to higher density qubit arrays than those based on isolated atoms or defects. An ideal meta-framework should be easy to synthesize, for example, through self-assembly driven by electrostatic interactions, hydrophobic effects,

π – π interactions, metal–ligand binding and/or high-yield covalent-bond formations (for example, those achieved with click chemistry). In addition, its structure, bond lengths and angles should be easy to modify to elicit specific molecular qubit structural motifs and explore non-traditional geometries, for example, meta-structures that can accommodate single qubits, qubit pairs or triads. Chemical synthesis can also exploit the use of chiral centres to provide easy gating functionalities that can be manipulated using circularly polarized electromagnetic radiation⁶⁹.

The establishment of specific meta-architectures for qubit placement should ensure rigidity to promote longer decoherence times, chemical robustness and some degree of ‘quantum isolation’ for qubits that are prepared in specific quantum states or entangled with selected neighbouring qubits. Proteins, DNA and RNA, through directed evolution or de novo design, are potentially powerful scaffolds for precisely tuning the spatial placement and orientation of the atoms or molecules that constitute the chemical qubits. These scaffolds can facilitate the control of the interactions between qubits, such as the spin-exchange coupling between two electron spin qubits⁴⁹. In principle, photoactive or switchable bridge molecules provide a convenient platform for changing both the sign and the magnitude of the magnetic exchange couplings between two spin qubits, enabling ultrafast state manipulation, changes in the polarization of individual qubits and modulation of their entanglement. For example, using phenylene bridges, the strength of the coupling can be reduced by a factor of 50 through torsional distortions around the single C–C bonds joining the phenyl groups¹⁰⁴. Electron spin qubits arranged into these arrays will experience multiple pairwise exchange couplings with nearest and perhaps even next nearest neighbour spins. However, further studies are required to correlate both the magnitude and sign of the exchange interactions with the spin topology and coherence times. Exchange interactions between molecular spin qubits can be measured using EPR spectroscopy in the weak exchange limit¹⁰⁵ and by variable-temperature magnetic-susceptibility measurements in the strong exchange limit¹⁰⁶.

Self-assembly on 2D surfaces through non-covalent interactions and coordination chemistry also enables direct control over inter-qubit distances and the interactions responsible for entanglement

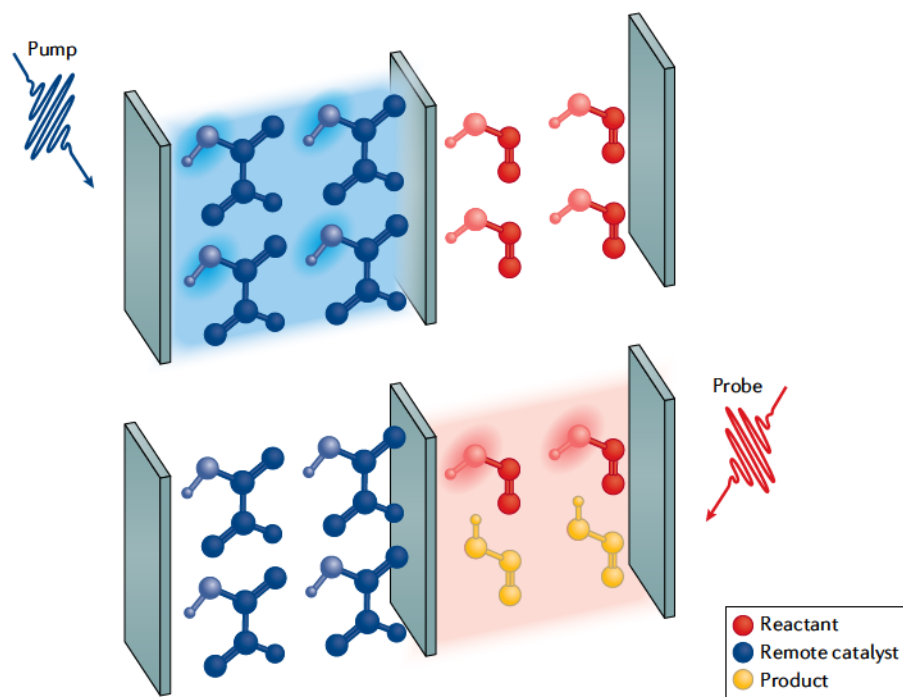


Fig. 2 | Remote control of chemical properties using optical microcavities. The quantum state of molecules in one cavity may affect the reactive outcome of molecules in another. The figure shows two coupled cavities that enable remote control of the infrared-induced conformational isomerization of the nitrous acid (HONO). These effects depend on the formation of polaritons, which are pseudo-particles formed by strong light–matter interactions aided by placing the molecule in a micro-cavity or a nanocavity. First, an infrared pump laser pulse impinging on the mirror of the remote catalyst cavity containing glycolic acid excites a polariton, the character of which is dominated by the remote catalyst cavity and the strongly coupled OH stretch (light-blue bond) of the glycolic acid (top). Second, a probe pulse can now efficiently excite a polariton, the character of which is dominated by the reactant cavity and the strongly coupled OH stretch (light-red bond) of the *cis*-HONO reactant, which subsequently converts into the product molecule (in yellow) *trans*-HONO. Similarly, coupled cavity arrays could be constructed to realize quantum gates and operations in the service of chemistry (bottom). Adapted with permission from REF.¹⁰³, Elsevier.

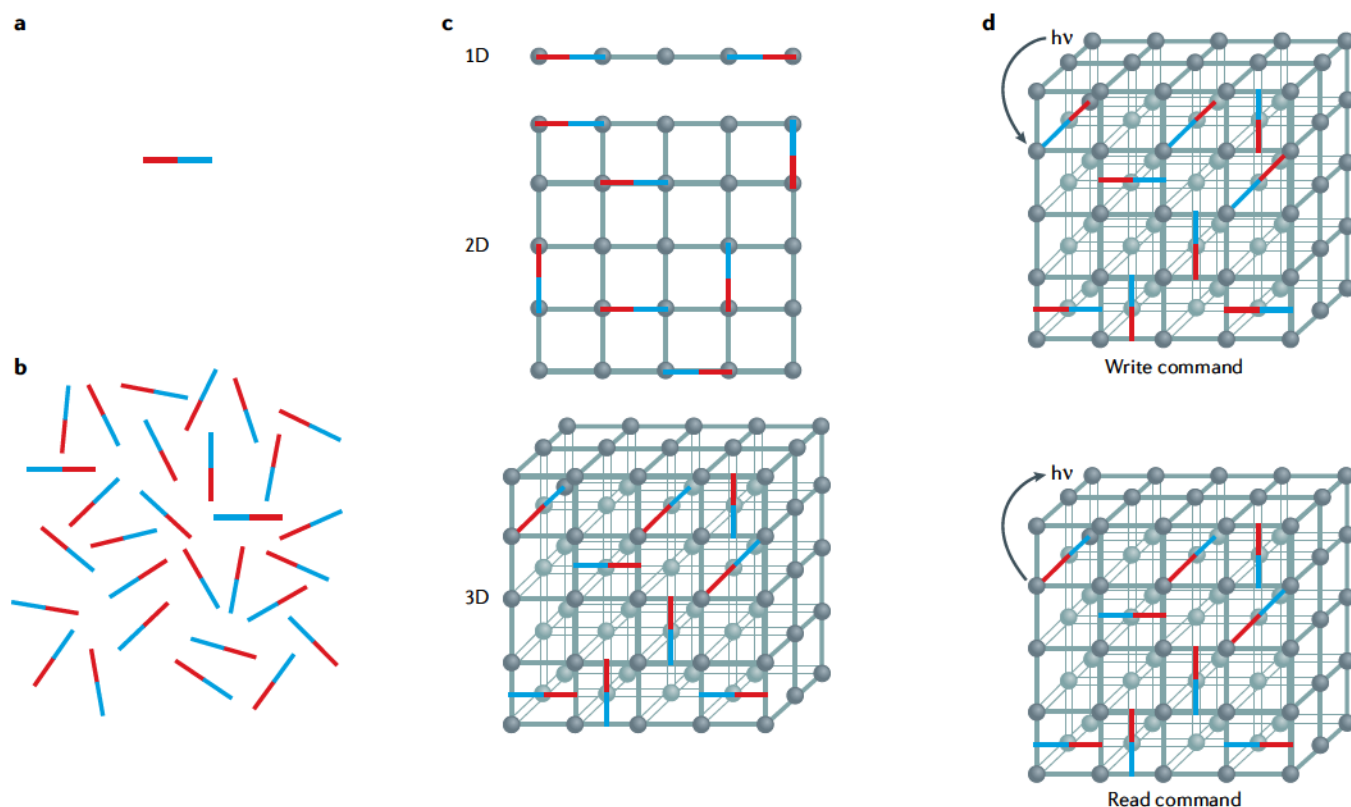


Fig. 3 | Assembly of molecules to meta-structures for applications in quantum information science. **a** | An isolated qubit prepared in a 'pure' quantum state. **b** | An array of randomly ordered qubits as might be found in liquid solution or in a frozen glass. **c** | Organization of isolated qubits in 1D, 2D or 3D meta-architectures. These scaffolds must serve to orient the qubits while simultaneously insulating them from each other, for example, to minimize the crosstalk between the prepared states. **d** | A light source can be

used to execute a 'write command' (top). Polarized light can be used to perform the command on the x, y or z axes of the meta-structure. Note the 'flip' of the qubit state as a result of the write command. A read command is also orientation-specific (bottom). The qubits themselves can be electron or nuclear spins, while the use of photons for writing and reading leads immediately to strategies for sensing, computing and long-range, quantum-encrypted communication.

between qubits¹⁰⁷. An advantage of lower-dimensionality meta-frameworks is that qubit arrays can be more easily isolated to minimize crosstalk¹⁰⁷. For example, a series of 1D structures consisting of alternating qubits and insulators can be staggered so that the resulting 2D and 3D structures consist of isolated 1D qubits¹⁰⁸ (FIG. 3).

Chemical approaches can also contribute to isolating qubits from environmental-noise sources that destroy coherence. Topological phases of matter have been at the forefront of numerous developments in solid-state physics during the past several decades¹⁰⁹. Interestingly, a predecessor in these studies was of much interest to chemists in the 1980s, when solitons — single waves that maintain their shape during their propagation — were predicted to emerge in long polyacetylene chains with defects that separated two (topologically) different insulating phases of the polymer¹¹⁰. Additional topological materials that might be employed for quantum noise isolation are so-called

Weyl materials, chiral materials in which angular and linear momenta are coupled for electrons conducted through them^{69,111,112}. The appeal of topological states lies in the fact that they are associated to the existence of robust quantum states that are immune to material imperfections or energetic disorder. For instance, quantum Hall systems are characterized by unidirectional current-carrying states at the edge of the material, which remain delocalized, even in the presence of impurities or static disorder¹¹³. Molecular analogues of these systems are currently underdeveloped, despite their apparent appeal in terms of achieving robust behaviours in complex systems that seemingly defy control. One notable example is the metal–organic framework Cu(1,3-benzenedicarboxylate) (Cu(1,3-bdc)), which is a topological magnon insulator¹¹⁴. Topological insulators have been proposed in the context of electrons in metal–organic frameworks¹¹⁵, as well as in excitons and polaritons in molecular aggregates^{116–118}. Typical features of topological insulators, such

as Dirac cones, have been experimentally observed as a result of the anisotropic polariton dispersions in aligned carbon nanotubes¹¹⁹ or organic molecules¹¹⁸ placed in optical microcavities. We expect many more examples to emerge in the next few years, such as the design of a Majorana fermion (a particle that corresponds to its own antiparticle), excitations in collective molecular degrees of freedom¹²⁰ and the emergence of anyonic statistics, which generalize fermionic statistics to exchange phases different from π (REF.¹²¹).

In a similar vein, the multi-entangled ground state of a spin liquid, for example a multi-spin system with quantum entangled spins, is posited as an excellent platform for QIS. There are two pathways to the realization of a spin liquid in a 2D system: through geometric frustration or the Kitaev model, in which the spins are positioned on the vertices of a honeycomb lattice¹²². Within both pathways, precise control over the geometric relationship between sites enables a multi-entangled ground state. Organic, hybrid metal–organic and inorganic

synthetic approaches all offer promise for the creation of new spin liquids. Indeed, most of the top candidates for spin liquids are observed in triangular lattices of stable organic radicals¹²², inorganic compounds such as herbertsmithite¹²³ and metal–organic hybrids such as Cu(1,3-bdc)¹¹⁴.

Measurement of molecular QIS systems

A crucial part of exploring quantum information encoded in molecular systems is related to the development of experimental techniques that incisively reveal quantum behaviour, non-classical correlations or function stemming from quantum correlations such as entanglement¹²⁴ or discord¹²⁵. These experiments will, in turn, inform us, for example, on how to influence charge transport, new state separations or catalytic transformations relevant to energy applications. We envision three principal directions. First, we need to devise general approaches for detecting quantum discord — that is, the amount of non-classical correlation — in systems for which we do not know a priori how this is manifested. Second, it will be productive to use strategies developed in quantum optics to design powerful spectroscopic experiments that measure statistics of photon numbers or exploit entangled photons. Third, we should build on advances in multidimensional ultrafast spectroscopic methods that, for instance, probe off-diagonal elements of relevant density matrices through coherent oscillations¹²⁶.

Entanglement is not necessarily black and white. There are degrees of entanglement and it is now suspected that a system hosting even small amounts of non-classical correlations can provide a useful quantum-information resource¹²⁴. For example, scaling the number of entangled qubits to near-macroscopic proportions can inform us about the boundary between quantum and classical correlations. Discovering quantum phenomena in the form of non-classical correlations in complex molecular systems will likely require us to detect and characterize subtle — perhaps hitherto unknown — correlations that defy classical interpretation. How do we go about this in a practical way that can be applied to complex molecular systems where quantum information may be well hidden? If we can succeed in demonstrating such experiments to reveal quantum information, there are several questions that can be addressed, including the quantification of quantum effects in biological or other complex systems. Also, we could determine how to prepare and manipulate states in ‘imperfect’

materials (for example, organic films) or the use of complex systems for secure encryption.

In terms of developing these experiments, we can ask how we might deploy quantum-optics measurements to detect quantum correlations. For instance, experimental studies suggest the advantage of moving from measuring the average spectroscopic signal — the expectation value of the number operator in the shot-noise limit — to recording distributions so that quantum correlations can be revealed^{127,128}. The use of non-classical light sources to probe quantum behaviour in new spectroscopic measurements will also be a promising approach¹²⁹. Techniques that have been developed to characterize non-trivial quantum correlations, like quantum discord, might inspire new experiments. Quantum discord is measured by calculating the difference between two distinct measurements of the same mutual information (conditional probability)¹²⁵. Analogous experiments, if devised, could uncover quantum discord¹²⁵ embedded in complex molecular systems. This will help pinpoint robust quantum information that is unique to these scenarios and exploit it to uncover new functionality.

Ultrafast spectroscopy that uses sequences of ultrashort pulses (typically ~10 fs) to prepare coherent superpositions of electronic and vibrational states and interrogate the ensuing dynamics has

been a productive, ground-breaking approach for the study of complex molecular systems (FIG. 4). The current state of the art for probing electronic and vibrational coherence is multidimensional coherent spectroscopy, which extends the sophisticated multidimensional approaches developed in magnetic resonance to the infrared and UV–visible regimes and can help characterize properties of the ensemble density matrix¹³⁰. These multidimensional spectroscopic approaches have, for example, provided insight into energy transfer and transduction processes in photosynthetic systems^{126,131}, and have demonstrated that the mixing of electronic and vibrational states can prolong coherence-dephasing times in molecular systems^{132–135}.

Data from ultrafast laser experiments are subject to ensemble dephasing, which might obscure coherence phenomena intrinsic to systems within the ensemble, motivating recent efforts to reach single-molecule accuracy^{136–138}. Despite the low intensity of non-linear optical signals, fluorescence-detection approaches^{136,137} and recent single-molecule pump–probe experiments¹³⁸ have put this goal within reach.

Coherent spectroscopies have proved powerful, but the broader toolbox of quantum measurement has not yet permeated the chemistry community. New spectroscopies could exploit measurement principles such as non-demolition, weak or projective measurements that collapse

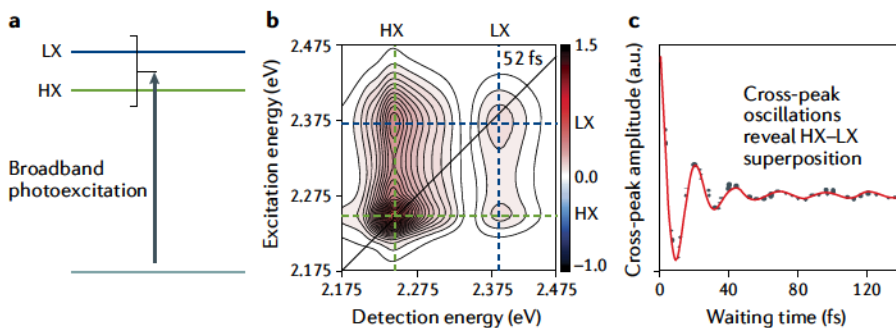


Fig. 4 | Ultrafast spectroscopy using sequences of ultrashort pulses prepares coherent superpositions of electronic and vibrational states. **a** | Level diagram showing the way a femtosecond broadband laser pulse excites a superposition of exciton states, specifically the heavy-hole (HX) and light-hole (LX) exciton transitions of CdSe nanoplatelets. An electronic wave packet is produced that comprises a quantum superposition of the exciton states. **b** | 2D electronic spectrum recorded at a pump–probe delay time $T = 52$ fs. The 2D electronic spectrum enables us to study the ultrafast dynamics and, more specifically, temporal evolution of coherences produced by photoexcitation. The third-order radiated signal resulting from the interaction of the sample with three broadband femtosecond pulses is heterodyne detected and recorded as a function of the pump–probe delay time T (waiting time). For each T , a 2D map of the signal amplitude as a function of the detection energy and of the excitation energy is plotted. The evolution of the peaks in amplitude and shape reveals information about the dynamics of the system and its interaction with the environment. **c** | Amplitude oscillations in the lower cross peak of the repasing 2D spectrum for a CdSe–CdZnS nanoplatelet (real part with population relaxation subtracted) as a function of the waiting time reveals the quantum superposition as oscillations. Parts **b** and **c** are adapted from REF.¹³⁵, Springer Nature Limited.

the wave function¹³⁹. Furthermore, concepts of quantum metrology¹⁴⁰, which exploit enhanced detection sensitivities arising from non-classical correlations of light sources, could be used to design better analytical-chemistry protocols. We anticipate many developments along these lines in the next few years.

The large range of possible molecular QIS systems based on electronic states, electron spins and nuclear spins mandates novel integrated experimental techniques that can simultaneously probe and manipulate all these degrees of freedom using quantum optics combined with fully coherent pulse magnetic resonance spectroscopy (EPR and NMR) using linear and circularly polarized light. Recent advances in spin-manipulation technologies such as shaped microwave pulses^{141,142} and optimal control techniques¹⁴³ present opportunities to manipulate electron and nuclear spins with tremendous precision and open the way to new and as yet unexplored preparation, manipulation, transport and readout schemes for QIS. These types of technologies might also enable new chemical applications, such as reaction-yield control through quantum coherence¹⁴⁴.

The use of quantum-entangled photons in the measurement of the optical properties of molecules and biological systems is an important emerging area of research¹⁴⁵. Photons can be entangled with different degrees of freedom: their wave vector, frequency, time, phase or polarization¹²⁹. In addition, entangled photons can provide greatly enhanced capabilities for chemical detection¹⁴⁶, imaging¹⁴⁷, microscopy¹⁴⁸, lithography¹⁴⁹ and tomography¹⁵⁰.

The first reports of the use of entangled photons as spectroscopic tools were the prediction and experimental verification of linear rather than quadratic scaling of two-photon absorption rates with the pump photon intensity¹⁵¹. The experimental verification of this effect in atoms¹⁵², molecules^{153,154} and biological systems¹⁴⁵ established entangled photons as powerful sources for non-linear spectroscopy with low photon fluxes. Additionally, observation of the non-monotonic quantum interference of entangled two-photon absorption suggested a two-photon transparency effect unique to entangled excitation processes^{155,156}. This result has prompted new theoretical predictions suggesting that two-photon spectra resulting from the use of entangled photons in 2D spectroscopy scale linearly rather than quadratically with laser field intensity, which enables measurements at low powers^{157,158}.

Computational methods in chemical QIS

Fabrication, properties and functions of molecular qubits are affected by a variety of factors, and advanced computational approaches are needed to address challenges related to the coupling of various electronic degrees of freedom and their impact on coherence and decoherence effects, control of excited states, tunability and understanding entanglement processes in optically prepared states. A separate class of methodologies is needed to describe molecular qubits under operating conditions beyond idealized models, in which disorder, fluctuations and interactions with the external environment are not properly considered.

The computational study of the above-mentioned effects requires more than a single class of methodologies and seamless integration of quantum-mechanical and classical degrees of freedom to tackle systems and processes at various length scales and timescales, while maintaining an accurate model of the underlying basic interactions. The description of the quantum effects that characterize the interactions of molecular systems with external fields and excited states will also require state-of-the-art electronic-structure methods and strategies. Computational protocols need to connect various representations of many-body phenomena involving wave functions, density matrices, electron densities and self-energy parameterizations (BOX 4).

A description of the spin properties of electronic states identified as candidates for molecular qubits will require the inclusion of various interactions, such as coupling to external fields, hyperfine interactions, spin-orbit coupling, magnetic spin exchange and other relativistic effects. The proper treatment of these interactions will enable the development of accurate interaction-based models that, in turn, will address how these interactions can be used to control quantum states and decoherence timescales.

Methodologies for the theoretical description of excited-state processes should aim for an accurate description of correlation effects over large regions of potential energy surfaces (PESs) associated with the processes of interest. In many cases, changes in the geometrical structure of molecular systems induce significant modifications to the corresponding wave functions. For processes involving single excitations associated with forming electron-hole pairs, low-order methods stemming from time-dependent density functional theory (DFT), real-time DFT

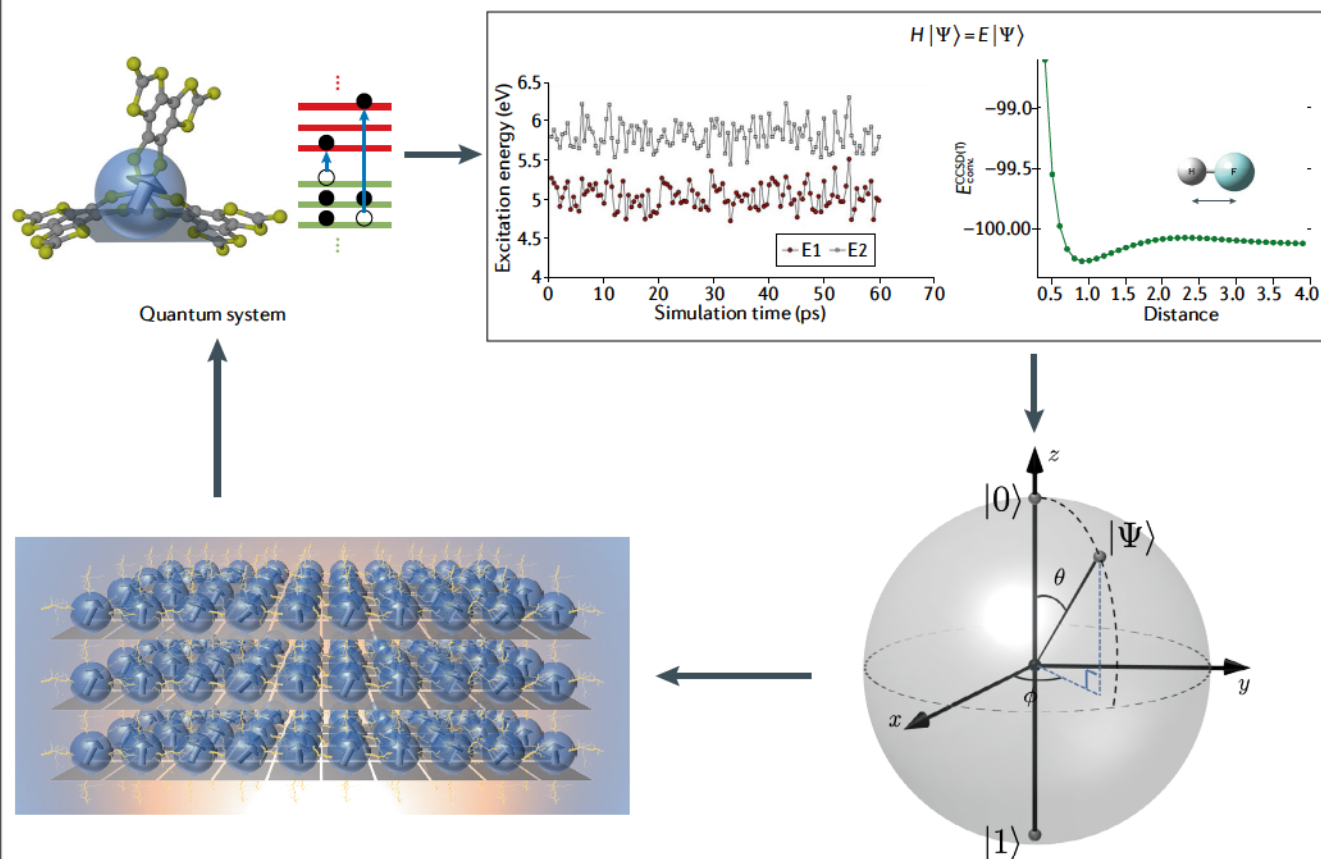
and low-rank configuration-interaction methods may provide a satisfactory level of accuracy¹⁵⁹. However, for more complicated situations corresponding to topological events on the PESs such as transition states, avoided crossings and conical intersections, formalisms providing a hierarchical structure of approximations for the systematic inclusion of higher electronic excitations are needed. Several methodologies have been extensively developed over the last decade that can address these challenges by significantly extending the applicability of low-rank methods. These methods include multi-reference configuration interaction¹⁶⁰, density matrix renormalization group¹⁶¹, equation-of-motion coupled cluster^{162,163}, Green's function^{164–166} and multi-reference many-body perturbation-theory formalisms^{167,168}. These methodologies not only provide a thorough characterization of the wave functions in terms of entanglement effects but also offer increased levels of accuracy. Several processes associated with excited-state energy transfer, photoisomerization processes, and formation and evolution of excitons and excitonic polaritons require efficient implementations of analytical gradients to enable searches on PESs and elements of adiabatic and non-adiabatic dynamics.

As has been demonstrated in recent years, the methodologies mentioned in the preceding paragraph can be universally applied to describe electronic states in various energy regimes, ranging from UV to X-ray excitations. However, given the size and complexity of condensed-phase molecular processes, a significant effort will be required to build practical multiscale computational methods that use high-accuracy methods to describe fragments of the composite systems where significant modifications of the wave function occur and where the proper inclusion of correlation effects plays a crucial role. In recent years, integration of advanced many-body formulations, reduced scaling approaches and parallelization strategies enabled the development of reliable dynamical mean-field theories with coupled-cluster (CC) impurity solvers¹⁶⁹, finite-temperature Green's function methods^{170–172}, scalable CC Green's function implementations¹⁷³ and reduced-scaling CC and perturbative implementations for ground-state and excited-state simulations^{174–176} and self-energy calculations¹⁷⁷. Combinations of the computational approaches discussed

Box 4 | Theoretical approaches to molecular quantum information science

Theoretical studies begin with the selection of electronic-structure methods to understand ground-state and excited-state correlation effects that describe potential-energy surfaces. For processes involving single excitations associated with forming electron-hole pairs, low-order methods stemming from time-dependent density functional theory may provide a satisfactory level of accuracy¹⁵⁹. However, for more complicated potential-energy surfaces, formalisms providing a hierarchical structure of approximations for the systematic inclusion of higher electronic excitations are needed^{160–168}. These methodologies not only provide a thorough characterization of the wave functions in terms of entanglement

effects but also offer increased levels of accuracy. Simulations focus on time-dependent phenomena and interactions of quantum systems with the environment that play a critical role in entanglement and decoherence processes. Multiscale methodologies^{186–193} can address these questions to give meaningful simulations over appropriate time ranges to follow the complete system dynamics of spin qubits. Quantum many-body approaches at the spatial scales and timescales are used to describe properties of molecular qubits under operating conditions. The overall process is iterative and provides information to improve the design of individual molecular qubits^{195–197}.



Excitation energy versus simulation time graph is adapted with permission from REF.²¹⁰, AIP. ΔE correction versus distance graph is adapted with permission from REF.²¹¹, ACS.

in this section can provide reliable and practical computational frameworks to support experimental effort to design molecular quantum qubits.

New state-of-the-art experimental techniques have begun to probe matter at unprecedented length scales and timescales. For example, it has been shown that ultrafast, attosecond, multidimensional X-ray spectroscopy can probe the electronic structure and structural dynamics of molecules using their response to sequences of short pulses with variable delays, polarizations, wave vectors and controlled phases^{178–180}. In addition, these powerful techniques have been used to track electronic coherences in real time in atoms and diatomic molecules^{178–180}.

Even though decoherence phenomena in realistic complex systems has been amply explored with empirical and lower-order approaches^{181–185}, the deeper connection between decoherence and electronic correlation has not been explored in detail. It is natural to ask if these phenomena are, in some way, coupled. This entails performing molecular dynamics simulations using high-accuracy electronic-structure methods that account for electronic–nuclear couplings to understand how electronic correlation influences the couplings between the electronic and nuclear subsystems and, in turn, shed light on electronic decoherence. Extending these approaches to more complex molecular and materials structures requires theory

developments in electronic-structure methods, spectroscopies, non-linear optics and complex non-adiabatic molecular dynamics that need to consider spin–orbit and environmental effects.

A computational strategy should also capitalize on existing computational-chemistry infrastructure that provides scalable and interoperable environments for integrating various formalisms. This is especially important in the context of multiscale theories that provide a description of chemical processes in complex environments that can assist the study of the impact of linkers, ligand fields and external stimuli on decoherence of molecular qubits. Embedding methods such as various multiscale quantum-mechanics/

molecular-mechanics formalisms¹⁸⁶, methods of solving DFT Kohn–Sham equations in the presence of embedding potentials, wave-function-theory-in-DFT methods^{187,188}, the fragment molecular-orbital approach¹⁸⁹ and fast electron-correlation methods¹⁹⁰ are of special interest. Important progress in the development of reliable embedding schemes is associated with the use of the Green's function formalism¹⁹¹. Recently, the possibility of using highly correlated methodologies to describe local Green's functions or corresponding self-energies in dynamical mean-field theories has attracted considerable interest¹⁹². Several methods have also been employed to account for many-body correlation effects in self-energy calculations for impurity regions embedded in a surrounding bath¹⁹². There is a clear need for developing these methods, along with various types of computationally fast, reduced-scaling formalisms¹⁹³, in order to understand the relationship between system size and the coherence time of electronic states.

Interactions of quantum systems with environments also play a critical role in decoherence processes and for the loss of quantum information, which is commonly referred to as wave-function collapse¹⁹⁴. A detailed understanding of environmental contribution to decoherence is one of the most pressing issues on the way to practical realizations of quantum computers. Therefore, theoretical and computational approaches that can help to determine the impact of decoherence effects on molecular qubits are in demand. A powerful tool for analysing decoherence effects is the semigroup approach¹⁹⁵ and master equations for quantum systems obtained by averaging over environmental degrees of freedom. In this approach, the equations of motion involve the system operators, instead of the elements of the reduced density matrix¹⁹⁶, and provide a framework to combine many of the computational approaches discussed above. Moreover, recent advances in the description of open systems, quantum dynamics and quantum transport provide simple validation checks for molecular qubits¹⁹⁷.

The chemical complexity and timescales that need to be tackled in the design and characterization of molecular qubits will require a much larger dependence on molecular-dynamics simulations for interpretation and impact assessment. The difficulty of simulating these systems is greatly increased by the sensitivity of the processes from the atomic to the macroscopic scale. This includes unusual

bonding behaviours of the materials, the complex, defect-ridden, variable temperature and pressure environments likely to be encountered in operando, and the requirements that simulations be as parameter-free as possible and extremely reliable. Despite the continuous effort being devoted to improving the accuracy and efficiency of computational quantum methods, these tools will be of little value for the simulation of multi-qubit arrays without improvements in techniques to traverse and sample such a high-dimensional phase space. For example, the time range sampled in typical molecular simulations and that of chemical reactions can differ by as much as a factor of $\sim 10^{12}$. Current methods for exploring phase space are imperfect. For example, explicit time integrators for non-linear differential equations are not parallelized and require small time steps¹⁹⁸. Implicit time integrators show significant energy drift and free-energy methods need very large numbers of iterations to converge even simple processes¹⁹⁹. Also, search methods for complex processes require appropriate order parameters that are often unknown. We will require new methods for time integration²⁰⁰, efficient exploration of phase space^{201–203}, choosing order parameters²⁰⁴, as well as faster electronic-structure methods and more robust methods for developing approximate molecular-dynamics models that combine elements of machine-learning techniques²⁰⁵.

Outlook

We are optimistic that the upcoming years will witness much synergy between QIS and chemistry. Molecules provide versatile platforms for preparing multi-qubit arrays that will impact quantum computing and communication, as well as quantum sensing in complex condensed-phase and biological environments. Such molecular systems represent a middle ground between atomic and solid-state QIS architectures and will have significant impact on important societal challenges involving renewable energy and health care, in addition to the obvious application to information sciences. For example, understanding quantum coherence in molecular systems will have significant impact on fields such as energy production and storage, as well as catalysis for directing energy towards pathways that result in energy-efficient, environmentally benign synthesis of new molecules and materials. A key advantage of this approach is the ability to tailor molecular systems to specific applications

using the powerful synthetic methodologies that are intrinsic to chemistry. Further, the continuing development of new spectroscopic methods to probe electronic, vibronic, vibrational and spin-coherence phenomena bodes well for being able to understand quantum coherence in complex molecular systems and use it for QIS applications by applying these techniques to address and read molecular qubits. This new understanding will be greatly aided by new theoretical methodologies that will not only be able to accurately describe quantum phenomena in molecular systems but will also serve as predictive models for designing and preparing new molecular systems for QIS applications. Finally, QIS applications yet to be envisioned, which embrace the complexity and functionality of molecular systems, are limited only by our imaginations!

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