Optically addressable molecular spins for quantum information processing

S. L. Bayliss\textsuperscript{1,2}, D. W. Laorenza\textsuperscript{3,4}, P. J. Mintun\textsuperscript{1}, B. D. Kovos\textsuperscript{1}, D. E. Freedman\textsuperscript{2,5}, D. D. Awschalom\textsuperscript{1,3,4,6}

Spin-bearing molecules are promising building blocks for quantum technologies as they can be chemically tuned, assembled into scalable arrays, and readily incorporated into diverse device architectures. In molecular systems, optically addressing ground-state spins would enable a wide range of applications in quantum information science, as has been demonstrated for solid-state defects. However, this important functionality has remained elusive for molecules. Here, we demonstrate such optical addressability in a series of synthesized organometallic, chromium(IV) molecules. These compounds display a ground-state spin that can be initialized and read out using light and coherently manipulated with microwaves. In addition, through atomistic modification of the molecular structure, we vary the spin and optical properties of these compounds, indicating promise for designer quantum systems synthesized from the bottom-up.

Optically addressable solid-state spins (1–4) are an important platform for quantum information science, with impressive demonstrations ranging from quantum teleportation (5) to the mapping of individual nuclear spins (6). The optical-spin interface of these solid-state systems is crucial for a diverse range of applications, from nanoscale sensing to long-distance quantum communication, as it enables straightforward single-spin readout and initialization. However, for this family of qubits, synthetic tunability of optical and spin properties, deterministic fabrication of multifluqubit arrays, or translation of spin centers between different host materials and devices remain outstanding goals.

By contrast, chemical synthesis of molecular spin systems affords bottom-up qubit design (7, 8). A chemical approach offers tunability through atomistic control over the qubit; scalability through chemical assembly of extended structures; and portability across different environments (e.g., solution, surface, solid-state), because the qubit is not confined to a specific host. These capabilities provide substantial control over the intrinsic and extrinsic environment of molecular qubits. Notably, with chemical synthesis, nuclear spins can be controllably placed around a molecular qubit (9), arrays of spins can be created in one-, two- and three-dimensional architectures (10, 11), and molecular spins can be integrated into electronic and photonic devices (12, 13). Molecular systems have shown impressive capabilities, including long spin coherence times (14, 15), manipulation of photoexcited triplet states (16–18), and quantum optics with spin-singlet (\(S = 0\)) organic molecules (19). However, in contrast to spins in semiconductors, the ground-state spins of molecular systems have lacked an optical-spin interface for both qubit initialization and readout (20). Creating such an interface in a molecular platform would generate a class of qubits that can be engineered with atomic precision, with potentially transformative applications for bottom-up quantum technologies ranging from quantum sensors to hybrid quantum systems.

Here, we synthesize a series of molecular qubits with such an optically addressable ground-state spin. We show that these molecular spin qubits can be initialized and read out with light, and coherently manipulated with microwave fields. Notably, chemical modification of these qubits modulates the resulting optical-spin interface, illustrating the potential of bottom-up qubit creation for optically addressable spin systems.

To achieve the desired optical addressability, we target a molecular system consisting of a metal ion bonded to organic moieties (ligands), comprising a portable qubit of ~1-nm size. This metal-organic motif provides a well-defined qubit through the electronic spin of the central metal ion, and the surrounding ligands enable synthetic modification of the optical and spin properties.

The key requirements for such an optically addressable molecular spin qubit are (i) a ground-state spin that can be coherently manipulated and (ii) a spin-selective optical process to initialize and read out the spin. To achieve these functionalities, we selected a chromium ion (Cr\(^{4+}\)) coordinated by strong-field (aryl) ligands in a high-symmetry configuration, which gives rise to the energy-level structure shown in Fig. 1A. The \(d^0\) electronic configuration of Cr\(^{4+}\) in a pseudo-tetrahedral environment produces a spin-triplet (\(S = 1\)) ground state with a small ground-state zero-field splitting, characterized by the parameters \(D\) and \(E\) (Fig. 1A and fig. S1), allowing for spin manipulation at readily available microwave frequencies.

A strong ligand-field environment ensures that the lowest-lying electronic excited state is a spin-singlet (\(S = 0\)) (21). This configuration leads to narrow optical transitions between the \(S = 1\) ground state and the \(S = 0\) excited state, which, when combined with the ground-state zero-field splitting, enables optical spin readout and initialization (i.e., spin polarization) through spin-selective resonant excitation. First, optical readout of the ground-state spin is possible because a probed spin sublevel (e.g., \(|0\rangle\) in Fig. 1A) will give rise to more photoluminescence (PL) than the other spin sublevels (e.g., \(|\pm1\rangle\) in Fig. 1A). Second, optical polarization of the ground-state spin results when selective excitation, combined with spontaneous emission, transfers population from the probed to the other spin sublevels (22). This is referred to as optical pumping or hole burning. To accumulate spin polarization over multiple excitation and emission cycles, the ground-state spin-lattice relaxation time (\(T_1\)) must be much longer than the excited-state lifetime (\(T_{2\text{opt}}\)). These components are the key ingredients that we use to obtain the desired optical-spin interface.

With these criteria in mind, we synthesized three Cr\(^{4+}\) compounds (Fig. 1B), which differ by the placement of a single CH\(_3\) (methyl group) on the coordinating ligands, through solution-phase chemistry. In brief, we react the appropriate aryl lithium species with Cr\(^{3+}\)Cl\(_3\) (THF)\(_3\) at \(-78°C\), which undergoes a disproportionation or auto-oxidation to yield the corresponding tetrahedral Cr\(^{4+}\)R\(_4\) [R = o-tolyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl; see (23) for further details] (24). We diluted each compound in their \(S = 0\), isoostructural tin analogs to form dilute molecular crystals (1, 2, 3), illustrated in Fig. 1C, thus reducing interactions between Cr\(^{4+}\) centers. The metal-center symmetry in these crystals varies from relatively high, \(S_4\) for 1, to low, \(C_3\) for 3, directly affecting the ground-state spin structure (23).

All experiments were performed on 1–3 in an optical cryostat with microwave access [\(+4\) to 5 K at the sample mount, Fig. 1C and (23)] unless stated otherwise.

Under off-resonant excitation (785 nm), ground-state population is promoted to the first \(S = 1\) excited state, undergoes fast intersystem crossing to the \(S = 0\) state, and decays to...
the $S = 1$ ground state, emitting near-infrared PL. For 1–3, this emission comprises sharp zero-phonon lines (ZPLs) ranging from 1009 to 1025 nm (Fig. 1D), along with longer-wavelength phonon sidebands. The minor ligand modifications in 1–3 also result in distinctive ground-state spin structures, as observed in ground-state electron spin resonance (ESR) measurements (Fig. 1G), with extracted values of $D$ and $E$ lying in the readily addressable regime of <5 GHz for each compound [because the signs of $D$ and $E$ are not determined and only their magnitudes influence our experiments, we take $D, E > 0$ for clarity (29)]. These features, along with optical lifetimes (3.3 to 6.9 µs, Fig. 1F) that are much shorter than $T_1$ [see below and (23)], therefore suggest that 1–3 satisfy the above criteria for optically addressable molecular qubits while exhibiting variable optical and spin properties.

To further confirm the level structure in Fig. 1A, we measure the emission of 1 under a high magnetic field using off-resonant excitation (Fig. 1E). Owing to the $S = 0$ excited state, the Zeeman splitting of the ground state manifests directly as a shift in the optical emission energies. This effect is clearly shown by taking the difference in PL spectra at 9 T: Optical emission into the $|±1\rangle$ spin sublevels shift to lower and higher energies, giving characteristic peaks on either side of the zero-field ZPL in the differential spectrum (Fig. 1E), along with a central dip [the feature at 1030 nm arises from the vibrational sideband (29)].

To demonstrate an optical-spin interface in these systems, we focus on 1 as an illustrative example before discussing 2 and 3. Using a narrow-line laser, we resonantly excite the $S = 1$ ground state to the $S = 0$ excited state (Fig. 2A) and collect emission into the phonon sideband to remove excitation laser scatter. First, we characterize the emission as a function of the excitation wavelength (Fig. 2B), showing a ZPL at 1025 nm: We excite at this ZPL...
maximum (dashed line Fig. 2B) for all following experiments. To further maximize emission, we align the excitation polarization with the optical dipole transition, which is collinear with the long axis of the needle-like crystal (Fig. 2B, inset). The optical inhomogeneous linewidth of ≈150 GHz shown in Fig. 2B is >>D and thus appears prohibitive for spin-selective excitation; however, resonant excitation addresses only a subensemble of molecules from the inhomogeneous distribution. Whereas the inhomogeneous linewidth is broadened by static energy-level variations, likely caused by strain, the subensemble linewidth is limited only by dynamical processes (e.g., electron-phonon coupling) (25). To demonstrate that the subensemble linewidth is indeed much narrower than the inhomogeneous linewidth, we compare the phonon sidebands under resonant excitation and off-resonant excitation (Fig. 2C). The emission line narrowing (26) under resonant excitation indicates that the ensemble ZPL indeed consists of narrower subensembles, which we use for all following spin-selective experiments.

We next measure all-optical initialization and readout of the ground-state spin using hole burning and recovery. To initialize the spin, we apply the pulse sequence outlined in Fig. 2D, consisting of a long optical pulse (2 ms) followed by a wait time (2 ms) to equilibrate ground-state spin populations before the next pulse. The emission during the optical pulse shows the characteristic behavior of optical spin polarization: a gradual drop in emission as population is pumped from the probed ground-state spin sublevel (the “bright” state) and into the other (“dark”) spin sublevels. The optical contrast between the start and the end of the pulse places a lower bound on the spin polarization of 14% (23).

Using this spin initialization, we measure the ground-state spin-lattice relaxation time, $T_1$, by performing the two-pulse experiment outlined in Fig. 2E. This sequence consists of an initialization pulse (300 μs), a variable relaxation time, and a readout pulse (20 μs). The initialization pulse transfers population to the “dark” spin sublevels. As ground-state spin population relaxes back to the “bright” sublevel, the emission increases. Measuring this emission at variable relaxation times yields $T_1 = 0.22(1)$ ms. That $T_1$ is much longer than the optical lifetime ($T_{\text{opt}} = 3.3$ μs, Fig. 1F) confirms that many optical cycles can be used to accumulate ground-state spin polarization.

We next manipulate the ground-state spin of 1 using a microwave field. First, using continuous-wave (cw) optical excitation, we place a subensemble of spins in the “dark” state and monitor changes in emission ($\Delta P/L$) as we sweep the microwave frequency. When this microwave frequency matches the spin sublevel splitting, the “dark” and “bright” sublevels are mixed, resulting in increased PL. Figure 3A shows this optically detected magnetic resonance (ODMR) as a function of both microwave frequency and optical readout. In these pulsed ODMR experiments, the wait time (10 μs ∼ 37 opt) between initialization and microwave manipulation ensures population is in the ground state prior to coherent control. This wait time, along with the above agreement between the ODMR and ESR spin parameters, shows that we coherently control the ground-state spin. Furthermore, the measured $T_2^*$, likely limited by the surrounding hydrogen nuclear spins, is comparable to other transition-metal–based molecular qubits in nuclear-spin-rich environments (15, 27), and we expect that ligand deuteration should greatly enhance $T_2^*$ (27, 28). Thus, with 1, we demonstrate optical initialization, microwave coherent control, and optical readout of the ground-state spin in an ensemble of molecular qubits.

Having demonstrated an optical-spin interface and coherent spin control for 1, we highlight how this functionality is not specific to a single compound. In Fig. 4, we show optical initialization, microwave spin manipulation, and optical readout of 2 and 3 through cw-ODMR. As captured by the simulations, the variable peak intensities arise from ESR selection rules (23). Notably, the additional ligand methyl groups in 2 and 3 lead to substantial $E$ by lowering the crystal symmetry, relative to 1, indicating that noise-insensitive (i.e., clock-like) transitions could be used to enhance spin coherence in these compounds (29). These results also suggest that modification of the host material provides a further opportunity to manipulate ground-state spin structure. Compounds 1 to 3 illustrate that minor synthetic modifications provide variable
magnetic and electronic structures, indicating potential for designing compounds with multiple, separately addressable qubit sites.

Although small molecular ensembles may find applications for quantum sensing, extension of these results to the single-molecule level will be important for their implementation as qubits. We anticipate single-molecule sensitivity could be achieved by reducing radiative lifetimes through coupling to a photonic cavity and enhancing photon collection efficiency. Furthermore, we expect that initialization and readout fidelities could be improved by enhancing the spin selectivity of the optical excitation. Such enhancement could be achieved by engineering compounds with larger zero-field splittings or narrower sub-ensemble optical linewidths (29).

We envisage several promising avenues for optically addressable molecular spin systems, which may be more challenging to achieve with solid-state defects. First, multimetallic systems could be synthesized with interacting metal sites that exhibit distinct optical-spin interfaces, enabling both individual qubit addressability and multiqubit operations. Targeted nuclear spin placement around these interfaces, enabling both individual qubit addressability and multiqubit interactions, could be achieved by reducing radiative lifetimes through coupling to a photonic cavity and enhancing photon collection efficiency. Furthermore, self-assembly could facilitate integration with phononic or electronic devices (32).

Finally, the highly tunable nature of molecules offers promise for rationally designed properties tailored to a specific purpose, e.g., telecom emission for long-distance quantum networks, or strong spin-phonon interactions for hybrid quantum systems. These results highlight pathways to design and create quantum technologies from the bottom-up.

REFERENCES AND NOTES

1. M. Natoture et al., Science 312, 551–553 (2006).
2. D. D. Awschalom, R. Hanson, J. Wrachtrup, B. B. Zhou, Nat. Photonics 12, 516–527 (2018).
3. A. Gottscholl et al., Nat. Mater. 19, 540–545 (2020).
4. N. Chejnevska et al., Single spin resonance in a van der Waals embedded paramagnetic defect. arXiv:1906.05903 [cond-mat.mes-hall] (2020).
5. W. Pfaff et al., Science 345, 532–535 (2014).
6. M. H. Abobeih et al., Nature 576, 411–415 (2019).
7. A. Gaia-Arlo, F. Luis, S. Hill, E. Cabrera, P. J. O’Hern, Nature 576, 411–415 (2019).
8. J. Ferrando-Soria et al., Nat. Commun. 7, 11377 (2016).
9. C. E. Jackson, C. Y. Lin, S. H. Johnson, J. van Tol, J. M. Zadrozny, J. Am. Chem. Soc. 140, 12090–12102 (2018).
10. Y. Yanabass et al., J. Am. Chem. Soc. 140, 12090–12102 (2018).
11. U. Ortobere et al., Adv. Funct. Mater. 28, 1801695 (2018).
12. R. Vincent, S. Kytäjä, S. W. Wernsdorfer, F. Balestro, Nature 488, 357–360 (2012).
13. M. Oxborrow, J. B. Breene, N. M. Alford, Nature 488, 353–356 (2012).
14. K. Baden et al., Nat. Commun. 5, 5304 (2014).
15. J. M. Zadrozny, J. Niklas, O. G. Poliankov, D. E. Freedman, ACS Cent. Sci. 1, 488–492 (2015).
16. J. Wrachtrup, C. von Borczyskowski, J. Bernard, M. Orritt, R. Brown, Nature 363, 244–245 (1993).
17. J. Köhler et al., Nature 363, 242–244 (1993).
18. V. Fidiotou et al., Nat. Phys. 8, 596–600 (2012).
19. D. Wang et al., Nat. Phys. 15, 483–489 (2019).
20. M. Atzori, R. Sessoli, J. Am. Chem. Soc. 141, 11339–11352 (2019).
21. B. N. Figy, G. A. Mitchell, in Ligand Field Theory and Its Applications (Wiley-VCH, 2000), pp. 131–141.
22. W. F. Koehl et al., Phys. Rev. B 93, 035207 (2017).
23. See the supplementary materials.
24. S. U. Koschmieder et al., J. Chem. Soc. Dalton Trans., 3427–3433 (1990).
25. H. Reisen, Coord. Chem. Rev. 250, 1737–1754 (2006).
26. H. Reisen, E. Krauss, J. Chem. Phys. 97, 7902–7910 (1992).
27. A. Ardavan et al., Phys. Rev. Lett. 98, 057201 (2007).
28. A. Ardavan et al., npj Quantum Inf. 1, 15012 (2015).
29. M. Shidoq et al., Nature 531, 348–351 (2016).
30. G. Dutt et al., Science 316, 1332–1336 (2007).
31. K. M. Woyner, D. W. Laueressa, R. D. Schaller, D. E. Freedman, J. Am. Chem. Soc. 142, 14826–14830 (2020).
32. R. Chikkaraddy et al., Nature 535, 127–130 (2016).
33. S. L. Bayliss, D. W. Laueressa, P. J. Mintur, B. D. Koves, D. E. Freedman, D. D. Awschalom. Dataset for: Optically addressable molecular spins for quantum information processing. Zenodo (2020), doi: https://doi.org/10.5281/zenodo.3909747.

ACKNOWLEDGMENTS

We thank M. S. Fatafah for experimental suggestions and insightful discussions and C. P. Anderson, A. Bourassa, P. Deb, G. Smith, L. R. Weiss, M. J. Amud, K. A. Collins, and M. K. Woyner for helpful comments on the manuscript. We thank P. H. Oyla for technical support with the ESR measurements and R. A. Spoonburg for technical support with ICP-OES experiments. Funding: We acknowledge funding from ONR N00014-17-1-3026 and the MRSEC Shared User Facilities at the University of Chicago (NSF DMR-1420709). This work made use of the Caltech EPR facility, which is supported by the NSF (NSF-151940) and the Dow Corning Nano Education Program, which has received support from Northwestern University, the State of Illinois, and the International Institute of Nanotechnology. Metal analysis was performed at the Northwestern University Quantitative Bio-element Imaging Center. D.E.F. and D.W.L. gratefully acknowledged the U.S. Department of Energy (DE-SC0019356) for total support on synthesis, design of molecules and ensemble ESR measurements. Author contributions: S.L.B., D.W.L., P.J.M., and B.D.K. performed the measurements and analyzed the data. D.W.L. synthesized the compounds. D.E.F. and D.D.A. advised on all efforts. All authors contributed to the data analysis and manuscript preparation. Competing interests: S.L.B., D.W.L., P.J.M., B.D.K., D.E.F., and D.D.A. are inventors on patent application no. 63008589 submitted by the University of Chicago that covers chemically tunable optically addressable molecular-spin qubits and associated compounds. D.D.A. is inventors on patent application no. 10608589 submitted by the University of Chicago that covers chemically tunable optically addressable molecular-spin qubits and associated compounds. P.J.M. is a paid consultant to ARCH Venture Partners.

Data and materials availability: The data can be accessed via www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk. CCDC codes: 1929362, 1929359, 1929360, 1929356, 1929357, 1929358, and 1929363.

SUPPLEMENTARY MATERIALS

science.sciencemag.org/content/370/6522/13109/suppl/DC1

Materials and Methods

Supplementary Text

Figs. S1 to S10

Tables S1 to S6

References (34–61)

27 March 2020; accepted 2 November 2020

Published online 12 November 2020

10.1126/science.abb9352