Final Technical Report for DOE Project DE-SC0020260

Project Title:	A Route to Molecular Quantum Technologies Using Endohedral Metallofullerenes
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Executive Summary

This project focused on fundamental studies of metal-organic hybrid molecules, including endohedral metallofullerenes (EMFs) and related cage-like structures in which quantum information can be encoded into the magnetic (spin) states associated with lanthanide (Ln) atoms that are encapsulated within a protective organic shell. This approach promises advantages over other current magnetic qubit targets based on inorganic molecules and solids. First and foremost, the organic cage provides a rigid environment devoid of elements that possess magnetic nuclei (the ^{12}C nucleus is non-magnetic), thereby protecting the encapsulated atoms from well-known and stubborn noise sources – random vibrations and fluctuating magnetic fields due to nearby nuclei – that can easily erase fragile quantum information states. Equally important, this approach opens up the vast toolbox of organic molecular chemistry. This allows for large-scale synthesis of chemically identical species, with exquisite control over the quantum information states of the associated Ln atoms. Meanwhile, chemical functionalization of the periphery of the organic cage provides routes to scaling-up into more complex quantum systems via molecular self-assembly. Finally, the quantum resources that are attainable within a single molecule containing one or more Ln atoms with large magnetic moments (e.g., Gd^{3+} and Eu^{2+}) are considerable in comparison to inorganic transition metal counterparts. Synthetic efforts carried out under this project have demonstrated targeted tuning of the magnetic quantum states of encapsulated Ln ions. In one of the first investigations, engineering hyperfine clock transitions is demonstrated in Lu^{2+} molecules, with tunable operating frequencies up to ~10 GHz. The clock transitions provide protection against environmental magnetic noise (primarily due to nuclear spin diffusion), leading to enhanced coherence. Meanwhile, a subsequent study focusing on vibronic coupling identified strategies for engineering shifts in vibrational mode energies away from particular electronic states in order to reduce their impact on T_1 (spin-lattice) relaxation. More recent work on f^7 compounds (Gd^{3+}) has demonstrated a coherent population transfer protocol involving the $2S + 1 = 8$ Zeeman levels associated with the spin $S = {}^7/_2$ ion, paving the way towards implementation of well-known quantum search algorithms. Chirped microwave pulses have also been employed to achieve highly non-thermal spin populations, providing a novel all-microwave route to quantum state initialization. As such, the main goals of the project have been achieved and the findings have been published in prominent journals.

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1. Accomplishments

All the major accomplishments of the project have been written up and published in (or submitted to) refereed journals (see Section **3. Products Developed Under this Award – Refereed journal publications**); all publications are retrievable through DOE PAGES. Here, we provide some of the main results as short research highlights.

Clock Transition due to Massive Hyperfine Interaction in a Lu(II) Qubit

Electron spin coherence, important in quantum information science, can be significantly enhanced at so-called clock transitions (CTs) – optimal operating points that are immune to magnetic noise. CTs can be generated via the hyperfine interaction (HFI) between electron and nuclear spins in atoms. Maximizing this interaction to achieve optimum coherence and a desirable operating frequency in the microwave regime requires enhancing electron spin density at the location of the nucleus, which can be achieved using coordination chemistry.

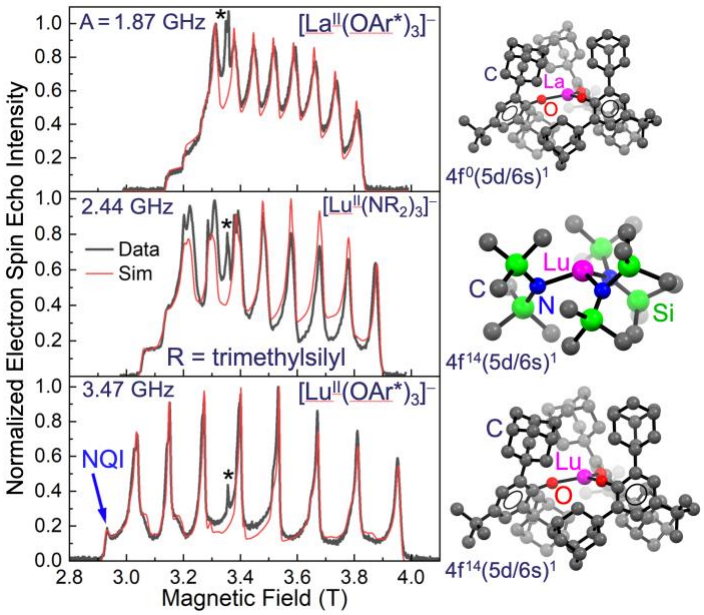

Fig. 1. Pulsed electron spin-echo spectra recorded at 94 GHz and 5 K, for the three compounds shown. The eight (= 2*I* + 1) lines arise due to the HFI with the *I* = $^7/_2$ ^{175}Lu or ^{139}La nuclear spin; the spacing between peaks is a direct measure of the HFI strength, A, which increases from top to bottom. The asterisk marks an impurity and the feature labeled NQI is attributed to a strong nuclear quadrupole interaction.

A family of molecules containing a single lanthanide (Ln = La or Lu) ion in the rare 2+ oxidation state was prepared. In each case, a single unpaired electron resides in a mixed 5d/6s orbital. The HFI can be controlled through choice of: (i) coordinating ligand, which tunes the s-orbital character and, hence, the spin density at the nucleus; and (ii) Ln ion, with increased orbital contraction for heavier Lu. As seen from the peak spacing in the high-field echo-detected ESR spectra (Fig. 1), significant control of the 5d/6s mixing is achievable, with [Lu^{II}(OAr*)$_3$]$^-$ exhibiting a massive 3.47 GHz HFI (c.f. < 100 MHz is typical for related molecules).

Hyperfine CTs are currently employed in more mature trapped ion quantum computers. This investigation demonstrates that the same approach is viable in molecular qubit platforms, giving rise to measurably enhanced coherence and prospects for future scalability via chemical self-assembly. The work was published in Nature Chemistry.

Vibronic Coupling in a 4f Molecular Magnet with Far-Infrared Magnetospectroscopy

Vibronic coupling, the interaction between molecular vibrations and electronic states, is a fundamental effect that profoundly influences a wide range of physical processes. In the

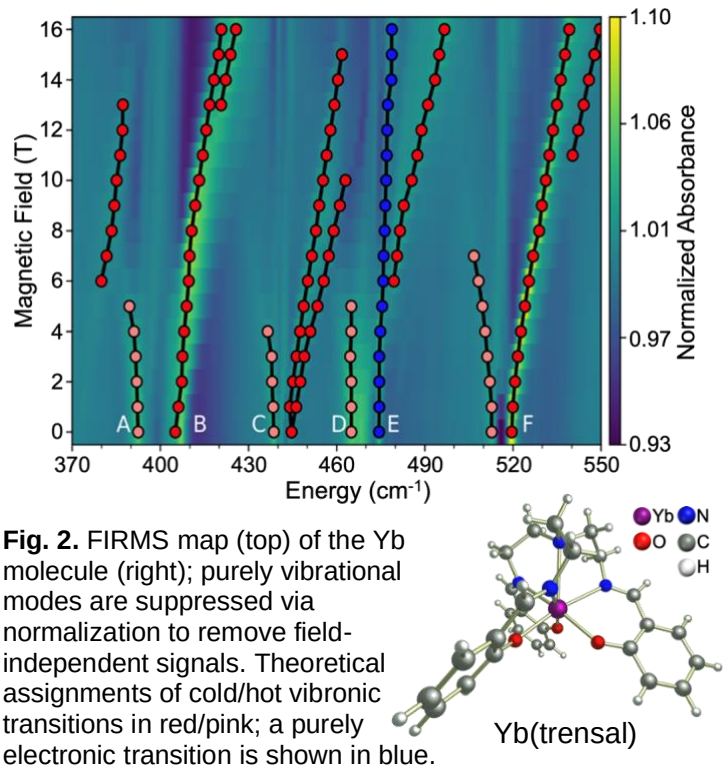

Fig. 2. FIRMS map (top) of the Yb molecule (right); purely vibrational modes are suppressed via normalization to remove field-independent signals. Theoretical assignments of cold/hot vibronic transitions in red/pink; a purely electronic transition is shown in blue.

case of molecular magnetic materials, it causes relaxation, which equates to loss of magnetic memory and loss of phase coherence in molecular spin qubits.

The study of vibronic coupling is challenging, and most experimental evidence is indirect. In this investigation, far-infrared magnetospectroscopy (FIRMS) was used to directly probe electronic transitions coupled to vibrational excitations in a metal-organic ytterbium(III) molecule (Fig. 2, right) that has attracted interest as a potential spin qubit. High magnetic fields enable a deconvolution of vibronic transitions that shift in energy due to the Zeeman interaction (Fig. 2, top) from a forest of much stronger electronic transitions that do not shift with field.

It is shown that vibronic coupling is strongest for vibrational modes that simultaneously distort the first coordination sphere (the atoms that coordinate directly to the ytterbium ion) and break the C_3 symmetry of the molecule. With this knowledge, vibrational modes can be identified and engineered to shift their energy towards or away from particular electronic states to alter their impact. Hence, these findings provide new insights towards developing general guidelines for the control of vibronic coupling in molecular spin qubits. The work was published in Nature Communications.

Inverse-Electron-Demand Diels-Alder Reaction for Fullerenes

Most EMFs have lower reactivities than empty fullerenes because they are more electron-rich, and therefore are not as reactive as electron acceptors. To make EMFs easier to functionalize for quantum information applications, we developed a new reaction, which has an inverse electron demand compared to normal cycloaddition reactions. Both the reactivity and regioselectivity of the reaction suggests more electron-rich molecules or motifs are more reactive. The initial work on the empty fullerenes, C_{60} and C_{70}, has been submitted to Organic Letters. Further, this reaction will be valuable in functionalization of EMFs that are traditionally inert towards common reactions.

Advances in Metallofullerene Chemistry

Advances in EMF chemistry are essential to their long-term viability in applications as molecular quantum materials. In recent years, new topics have emerged in EMF chemistry. First and foremost, new addition reactions were developed, notably some that are not based on known empty-fullerene reactions. Second, considerable progress has been made on regioselective multi-additions involving EMFs. Finally, EMFs have been

covalently conjugated with fullerene C_{60} to form functional materials. We summarized these new developments and discuss their implication for future directions for EMFs in the Chinese Journal of Chemistry (Wiley). Additionally, we published another review that covers the interactions between fullerene materials and biological systems.

Synthesis of First Molecularly Precise, Water-Soluble EMF Derivatives

EMFs are inherently hydrophobic and previous chemical modifications to make them water-soluble only led to mixtures of EMF derivatives with uncertain structures. We have developed a modular synthetic platform, dubbed "metallobuckytrio" (MBT), to selectively provide families of structurally well-defined, water-soluble EMFs with desired hydrophilic ligands. The new chemistry will help researchers access new materials design spaces. Although not described in our original proposal, their biomedical applications have been explored. Gd MBTs showed significantly higher relaxivity than any clinical MRI contrast agents, while preventing the toxic Gd^{3+} ions from leaking to physiological environments. EPR experiments performed at the National High Magnetic Field Laboratory confirmed the generation of Type I and Type II reactive oxidative species under light illumination, showing promise for photosensitizers in photodynamic therapy.

Decoherence Suppression in Gd(III) Spin Qubits

We have demonstrated that long phase memory times can be achieved in purely f-electron systems, e.g., Gd^{III}(trensal), which are essentially devoid of orbital angular momentum, hence local fluctuations of the ligand-field cannot couple magnetoelastically to the wave functions of the electronic system. These results broadly agree with previous studies on d- and f-shell molecular systems where isotropic states, devoid of orbital angular momentum, have been probed. Furthermore, the results agree with the study cited above on the magnetoelastic coupling in the isostructural (displaying thus the same phonon spectrum), but not isoelectronic Yb^{III}(trensal) complex. In the case of Gd^{III}(trensal) the coherent spin dynamics can be characterized by a phase memory time of 12 μs at 3 K, which is still detectable at temperatures up to 70 K. Based on these results, a general strategy for the optimization of coherence characteristics of molecular magnetic materials should be based on the minimization of the partial derivatives of all parameters entering the time dependent Hamiltonian of the system.

Slow Magnetic Relaxation in a Europium(II) Complex

Single-ion anisotropy is vital for the observation of slow magnetic relaxation in molecular lanthanide complexes. In the case of europium, the occurrence of this phenomena has been inhibited by the spin and orbital quantum numbers that give way to $J = 0$ in the trivalent state and the half-filled population of the 4f shell in the divalent state. By optimizing the local crystal field of a quasi-linear *bis*(silylamido) Eu^{II} complex, slow magnetic relaxation is observed for the first time in a molecule containing europium. The relaxation is dominated by a thermally activated mechanism, with an effective energy barrier of approximately 8 K, determined by bulk magnetometry and EPR. *Ab initio* calculations confirm second-order spin-orbit coupling effects lead to non-negligible, but otherwise highly axial magnetic anisotropy, splitting the ground state multiplet into four Kramers doublets, thereby allowing for the observation of an Orbach-like relaxation at low temperatures. This work has been accepted for publication in Nature Communications.

2. Summary of Project Activities During the Grant Period

The primary activities carried out under this project involved EMF purification and synthetic functionalization carried out at Rutgers University, followed by spectroscopic characterization using unique High-Field Electron Paramagnetic Resonance (HFEPR) tools available at the US National High Magnetic Field Laboratory (MagLab) at Florida State university. The synthetic and spectroscopic work was carried out primarily by students and postdocs supported by the project, under supervision of the PI and co-PI.

In addition to these activities, the project also involved development of enabling hardware in order to advance the spectroscopic goals of the project (reported under 2b). These developments have also been reported in a publication (see Section 3.0 – Products). Finally, the results from the project have been extensively disseminated in the form of talks presented at national and international conferences and workshops (listed under Section 2a. – Dissemination).

2a. Development

Broadband Fourier-Transform Detected EPR at W-band

We have developed a true wideband Fourier transform (FT) EPR detection capability at the uniquely high frequency of 94 GHz (W-band). It is based on the quasi-optical HiPER spectrometer, developed at the University of St. Andrews and located at the MagLab, into which we have integrated an arbitrary waveform generator (AWG) that is used to modulate the output from a solid-state multiplier chain prior to amplification, generating up to 1 kW microwave power with 1 GHz instantaneous bandwidth. Benchmark experiments have been demonstrated for standard samples. Using adiabatic chirp pulses, efficient (and fast) spin inversion is achieved, enabling frequency-dependent studies of the longitudinal magnetization recovery in the time-domain, again via chirp pulse echo detection. From such measurements, anisotropic spin-lattice relaxation time measurements can be performed in single shot mode. In addition, we implement the FT detection scheme for multi-dimensional (electron-electron double resonance, or ELDOR) experiments, demonstrating the full capabilities of the HiPER spectrometer. Finally, chirp pulses have also been employed to achieve highly non-thermal spin populations in f^7 electronic systems such as Gd^{3+} and Eu^{2+}, providing a novel all-microwave route to quantum state initialization.

2b. Dissemination

In the news: First and foremost, two publications resulting from this project (reported below under products, #1 and #3) have received further attention in a News and Views article in Nature Chemistry and a special virtual collection on f-block elements at www.nature.com. The details are as follows:

- *Molecular spins clock in*, News and Views story by Eric J. L. McInnes, Nat. Chem. **14**, 361 – 362 (2022); https://doi.org/10.1038/s41557-022-00919-y. Highlights our article: *9.2 GHz clock transition in a Lu(II) molecular spin qubit arising from a 3467 MHz hyperfine interaction,* Krishnendu Kundu, Jessica R. K.

White, Samuel A. Moehring, Jason M. Yu, Joseph W. Ziller, Filipp Furche, William J. Evans, Stephen Hill, Nature Chemistry **14**, 392 – 397 (2022); https://doi.org/10.1038/s41557-022-00894-4

- *Analysis of vibronic coupling in a 4f molecular magnet with FIRMS***,** Jonathan Marbey, Jon G. C. Kragskow, Christian D. Buch, Joscha Nehrkorn, Mykhaylo Ozerov, Stergios Piligkos, Stephen Hill and Nicholas F. Chilton, Nature Communications **13**, 825 (2022). Highlighted in Collection on f-block elements: https://www.nature.com/collections/highbeiiaj.

These two publications have also been highlighted on the National High Magnetic Field Laboratory homepage (https://nationalmaglab.org):

- https://nationalmaglab.org/user-facilities/emr/research/science-highlights/hyperfine-interaction-in-a-lu-ii-qubit/

- https://nationalmaglab.org/user-facilities/emr/research/science-highlights/vibronic-coupling-in-a-4f-molecular-magnet/

Impact: The two publications discussed above, as well as one other reported under products (publications #1, #3 and #6), have been discussed and cited in a recent National Academies of Sciences, Engineering and Medicine (NASEM) Report on *Advancing Chemistry and Quantum Information Science*, which was co-authored by the PI of this project:

- *Advancing Chemistry and Quantum Information Science – An Assessment of Research Opportunities at the Interface of Chemistry and Quantum Information Science in the United States*, Theodore G. Goodson III, David D. Awschalom, Ryan J. Babbush, Lawrence W. Cheuk, Scott K. Cushing, Natia L. Frank, Danna E. Freedman, Sinead M. Griffin, Stephen O. Hill, Hongbin Liu, Marilu Perez Garcia, Brenda M. Rubenstein, Eric J. Schelter, Michael R. Wasielewski, Damian Watkins, National Academies Press, Washington DC (2023). https://doi.org/10.17226/26850

The PI of this project also presented highlights of that report to the sponsors (DOE and NSF) and to congressional staffers, including results from the first publication above:

- **Virtual:** *Advancing Chemistry and Quantum Information Science – An Assessment of Research Opportunities at the Interface of Chemistry and Quantum Information Science in the United States*, Presented at Virtual Congressional Briefing on behalf of National Academies of Sciences, Engineering and Medicine, Theodore Goodson III, Stephen Hill, Marilu Perez-Garcia, Brenda Rubenstein, Michael Wasielewski and Linda Nhon, May 31, 2023.

- **Virtual:** *Advancing Chemistry and Quantum Information Science – An Assessment of Research Opportunities at the Interface of Chemistry and Quantum Information Science in the United States*, Presentation to the National Science Foundation and Department of Energy Chemistry Divisions, on behalf of National Academies of Sciences, Engineering and Medicine, Theodore Goodson III, Stephen Hill, Marilu Perez-Garcia, Brenda Rubenstein, Michael Wasielewski and Linda Nhon, May 25, 2023.

The PI also presented the same two project outcomes (publications #1 and #3 under Products) to a separate NASEM Committee tasked with preparing a decadal survey on *The Current Status and Future Direction of High Magnetic Field Science in the United States, Phase II*:

- **In Person:** *Electron Magnetic Resonance*, presented at National Academies of Sciences, Engineering and Medicine Committee on *The Current Status and Future Direction of High Magnetic Field Science in the United States, Phase II*, Information Gathering Meeting on September 29, 2023, at the National High Magnetic Field Laboratory, Session 3: *Spectroscopic and Imaging*. https://www.nationalacademies.org/event/40802_09-2023_the-current-status-and-future-direction-of-high-magnetic-field-science-in-the-united-states-phase-ii-meeting-on-9-29-2023

Tutorials: During the reporting period, the PI gave two tutorials at separate schools aimed at junior researchers:

- **Virtual:** *Directly observing quantum spin dynamics and relaxation via electron magnetic resonance*, 10th Annual Theory Winter School, National High Magnetic Field Laboratory, January 10 – 14, 2022.
- **In person:** *Electron Paramagnetic Resonance Spectroscopy and Quantum Spin Science*, Undergraduate School on Magnetism and Magnetic Materials, Florida State University, Tallahassee, FL, August 9 – 13, 2021.

Invited Talks: The PI and co-PI gave many invited talks during the reporting period in which they presented results from the project:

- *NAS Report on Advancing Chemistry & Quantum Information Science*, at the MagLab "New Frontiers" User workshop, Residence Inn, Tallahassee, FL, September 18, 2023.
- *Molecular Spin Clock Transitions*, Copenhagen Molecular Quantum Information Discussions, University of Copenhagen, Denmark, June 28 – 30, 2023.
- *Application of wideband pulsed high-frequency EPR to molecular quantum spin science*, 2023 Joint Current Trends in Molecular Nanomagnetism and North-America-Greece-Cyprus Conference, Spetses, Greece, May 8 – 13, 2023.

- **Keynote Lecture** *Molecular Spins for Next Generation Quantum Technologies*, National Quantum Technology Forum (NQTF), Clemson University, SC, April 14 – 15, 2023.
- *Molecular Rare Earth Clock Qubits*, 5th International Conference on Functional Molecular Materials (FUNMAT2023), Krakow, Poland, March 29 – 31, 2023.
- *Molecular Clock Qubits*, American Physical Society March Meeting, Las Vegas, March 5 – 10, 2023.
- *Molecular Spin Clock Transitions*, 2nd Workshop on Molecular Quantum Technology (MQT 2022), Puerto Natales, Chile, December 12 – 16, 2022.
- *Application of wideband pulsed high-field EPR to molecular quantum spin science*, International Conference on Molecular spintronics Based on Coordination Compounds: Toward Quantum Computer and Quantum Memory Device – 73rd Yamada Conference, Sendai, Japan, October 9 – 11, 2022.
- *Enhancing Coherence of Rare Earth Molecular Spin Qubits*, 44th International Conference on Coordination Chemistry (ICCC), Rimini, Italy, August 28 – September 2, 2022.
- *Rare Earth Molecular Clock Qubits*, Workshop at the 29th Rare Earth Research Conference (RERC29), Philadelphia, PA, June 26 – 30, 2022.
- *Clock Qubits*, Workshop at Telluride Science Research Center entitled "From Fundamentals of Molecular Spin Qubit Design to Molecule-Enabled Quantum Information", Telluride, Colorado, June 6 – 10, 2022.
- *Molecular Clock Qubits*, 9th North America Greece Cyprus Conference on Paramagnetic Materials, Ayia Napa, Cyprus, May 9 – 13, 2022.
- **Virtual:** 9.2 GHz Clock Transition in a Lu(II) Molecular Spin Qubit Arising from a 3467 MHz Hyperfine Interaction, at 49th Southeastern Magnetic Resonance Conference, Louisiana State University, October 22 – 24, 2021.
- **Virtual:** *Clock transition due to a record 1240 G hyperfine interaction in a Lu(II) molecular spin qubit*, virtual seminar at the 2nd joint webinar of the Association Française de Magnétisme Moléculaire and the Magnetism and Magnetic Resonance group of the French Society of Chemistry, June 24, 2021.
- **Virtual:** *Molecular Lanthanide Spins for Next Generation Quantum Technologies*, virtual talk at the Center for Molecular Quantum Transduction (CMQT) Annual Symposium, Northwestern University, May 6 – 7, 2021.
- **Plenary Talk (virtual):** *Controlling Electron-Nuclear Spin Couplings in Molecular Magnets*, virtual talk at the 54th Annual International Meeting of the ESR Spectroscopy Group of the Royal Society of Chemistry, hosted by the University of Cardiff, UK, Apr. 12 – 16, 2021.
- **Virtual:** *Probing Electron-Nuclear Spin Interactions via Broadband Pulsed EPR*, virtual presentation at the Intercontinental NMR Conference on Methods and Applications (ICONS2021), Feb. 10 – 12, 2021.

- **Virtual:** *Molecular Spins for Next Generation Quantum Technologies*, virtual presentation at the Workshop on Quantum Materials, University of South Florida, Jan. 29, 2021.
- *Magnetic Quantum Materials and High Field Electron Spin Resonance*, at the Workshop on Quantum Science, Eddleman Quantum Institute (EQI), UCLA Luskin Conference Center, CA, Mar. 6 – 8, 2020.
- *Molecular Spins for Next Generation Quantum Technologies*, at the Magnetism in North America (MAGNA) Conference, St. Simons Island, GA, Feb. 21 – 24, 2020.
- *Molecular Lanthanide Spins for Quantum Technologies*, at the 2nd Conference on Modern Trends in Molecular Magnetism (MTMM 2019), IISER Bhopal, India, Nov. 27 – 30, 2019.

Contributed Talks: The PI, co-PI and members of their research groups also gave many contributed talks during the reporting period in which they presented results from the project (* indicates presenter):

- *Controlling Quantum Spin Dynamics in Nanoscale Molecular Qubits*, S. Hill,* IBS Conference on Quantum Nanoscience, Ewha Womans University, Seoul, South Korea, October 10 – 13, 2023.
- *Tunable clock transitions in lanthanide complexes for quantum information technologies*, Jakub Hruby,* Krishnendu Kundu, Danh Ngo, Ryan Murphy, Randall McClain, Benjamin Harvey, Jeffrey R. Long, Stephen Hill, American Physical Society March Meeting, Las Vegas, March 5 – 10, 2023.
- *Spin Population Transfer in a Gd^{3+} Molecular Crystal Studied by Pulsed High-Field EPR*, Manoj Vinayaka Hanabe Subramanya,* Elvin Salerno, Miguel Gakiya, Krishnendu Kundu, Michael Shatruk, Stephen Hill, American Physical Society March Meeting, Las Vegas, March 5 – 10, 2023.
- *Pulsed 94 GHz EPR for Spin Population Transfer in a Gd(III) Molecular Crystal*, Elvin Salerno,* Manoj Subramanya, Miguel Gakiya, Krishnendu Kundu, Michael Shatruk, Stephen Hill, 50th Southeastern Magnetic Resonance Conference, Tallahassee, FL, Nov. 4 – 6, 2022.
- *Pulsed 94 GHz EPR for Spin Population Transfer in a Gd^{3+} Molecular Crystal*, Elvin Salerno,* Manoj Subramanya, Miguel Gakiya, Krishnendu Kundu, Michael Shatruk, Stephen Hill, 2nd Molecular Magnetism in North America (MAGNA 2022) conference, Gainesville, FL, May 1 – 4, 2022.
- *Massive 9 GHz Hyperfine Clock Transition in a Molecular Spin Qubit*, Krishnendu Kundu,* Jessica R. K. White, Samuel A. Moehring, Jason M. Yu, Joseph W. Ziller, Filipp Furche, William J. Evans, Stephen Hill, 2nd Molecular Magnetism in North America (MAGNA 2022) conference, Gainesville, FL, May 1 – 4, 2022.
- *Record 9.2 GHz clock transition in a Lu(II) molecular spin qubit arising from a massive 3467 MHz hyperfine interaction*, Krishnendu Kundu, Jessika R. K. White, Samuel A. Moehring, Jason M. Yu, Joseph W. Ziller, Filipp Furche, William J.

Evans, Stephen Hill,* at the ACS National Spring Meeting, San Diego, CA, March 20 – 24, 2022.

- *9.2 GHz Clock Transition in a Lu(II) Molecular Spin Qubit Arising from a Massive 3467 MHz Hyperfine Interaction*, S. Hill,* K. Kundu, J. White, S. Moehring, J. Yu, J. Ziller, F. Furche, W. Evans, American Physical Society March Meeting, Chicago, IL, Mar. 14-18, 2022.
- *Massive 9 GHz Hyperfine Clock Transition in a Molecular Spin Qubit*, Krishnendu Kundu,* Jessica White, Samuel Moehring, Jason Yu, Joseph Ziller, Filipp Furche, William Evans, Stephen Hill, 88th Annual Meeting of the Southeastern Section of the American Physical Society, Florida State University, November 18 to 20 (2021).
- *Massive 9 GHz Hyperfine Clock Transition in a Molecular Spin Qubit*, Krishnendu Kundu,* Jessica White, Samuel Moehring, Jason Yu, Joseph Ziller, Filipp Furche, William Evans, Stephen Hill, 49th Southeastern Magnetic Resonance Conference, Louisiana State University, October 22 – 24, 2021.

Poster presentations: The PI, co-PI and members of their research groups also gave many contributed talks during the reporting period in which they presented results from the project (* indicates presenter):

- *Tunable clock transitions in lanthanide complexes for quantum information technologies*, Jakub Hruby,* Krishnendu Kundu, Danh Ngo, Ryan Murphy, Randall McClain, Benjamin Harvey, Jeffrey R. Long, Stephen Hill, American Physical Society March Meeting, Las Vegas, March 5 – 10, 2023.
- *Wideband Fourier-Transform-Detected EPR at W-Band*, M.V.H. Subramanya,* J. Marbey, K. Kundu, J.E. McKay, S. Hill, 50th Southeastern Magnetic Resonance Conference, Tallahassee, FL, Nov. 4 – 6, 2022.
- *Tunable Clock Transitions in Lanthanide Complexes for Quantum Information Technologies*, J. Hrubý,* K. Kundu, D. Ngo, R. Murphy, K. R. McClain, B. G. Harvey, J. R. Long, and S. Hill, 50th Southeastern Magnetic Resonance Conference, Tallahassee, FL, Nov. 4 – 6, 2022.
- *Tunable Clock Transitions in Lanthanide Complexes for Quantum Information Technologies*, J. Hrubý,* K. Kundu, D. Ngo, R. Murphy, J. R. Long, and S. Hill, 43rd EPR Symposium at the 61st Rocky Mountain Conference on Magnetic Resonance, Copper Mountain, CO, July 25 – 29, 2022.
- *Spectroscopic Evidence of Spin-Phonon Coupling in an Yb(trensal) Single-Molecule Magnet*, Jonathan Marbey,* Jon Kragskow, Joscha Nehrkorn, Mykhaylo Ozerov, Nick Chilton, Stergios Piligikos, Stephen Hill, at the Magnetism in North America (MAGNA) Conference, St. Simons Island, GA, Feb. 21 – 24, 2020.

3. Products Developed Under this Award

Refereed journal publications (all are retrievable through DOE PAGES)

1. Krishnendu Kundu, Jessica R. K. White, Samuel A. Moehring, Jason M. Yu, Joseph W. Ziller, Filipp Furche, William J. Evans, Stephen Hill, *9.2 GHz clock transition in a Lu(II) molecular spin qubit arising from a 3467 MHz hyperfine interaction,* Nature Chemistry **14**, 392 – 397 (2022); https://doi.org/10.1038/s41557-022-00894-4
2. Yanbang Li, Thomas J. Emge, Antonio Moreno-Vicente, William P. Kopcha, Yue Sun, Iram F. Mansoor, Mark C. Lipke, Gene S. Hall, Josep M. Poblet, Antonio Rodríguez-Fortea, Jianyuan Zhang, *Unexpected Formation of Metallofulleroids from Multicomponent Reactions, with Crystallographic and Computational Studies of the Cluster Motion*, Angew. Chem. **60**, 25269 – 25273 (2021). https://doi.org/10.1002/anie.202110881
3. Jon G. C. Kragskow, Jonathan Marbey, Christian D. Buch, Joscha Nehrkorn, Mykhaylo Ozerov, Stergios Piligkos, Stephen Hill and Nicholas F. Chilton, *Analysis of vibronic coupling in a 4f molecular magnet with FIRMS***,** Nature Communications **13**, 825 (2022). https://doi.org/10.1038/s41467-022-28352-2
4. Yanbang Li, William P. Kopcha, Antonio Rodriguez-Fortea, Jianyuan Zhang, *Multicomponent Reactions Among Alkyl Isocyanides, sp Reactants, and sp^2 Carbon Cages*, Synlett. **33**, 907 – 912 (2022). https://doi.org/10.1055/a-1741-9000
5. Daniel A. Rothschild, William P. Kopcha, Aaron Tran, Jianyuan Zhang, Mark C. Lipke, *Gram-scale synthesis of a covalent nanocage that preserves the redox properties of encapsulated fullerenes*, Chem. Sci. **13**, 5325 – 5332 (2022). https://doi.org/10.1039/D2SC00445C
6. Manoj Vinayaka Hanabe Subramanya, Jonathan Marbey, Krishnendu Kundu, Johannes E. McKay, Stephen Hill, *Broadband Fourier-Transform Detected EPR at W-band*, Appl. Magn. Reson. **54**, 165 – 181 (2023). https://doi.org/10.1007/s00723-022-01499-3
7. Yue Sun, Cheng Qian, Thomas J. Emge, Yanbang Li, William P. Kopcha, Lu Wang, Jianyuan Zhang, *Synthesis of [60]- and [70]Fullerene-Fused Tetrahydroquinoxaline Derivatives by Oxidative [4 + 2] Cycloaddition with Unusual Reactivity and Regioselectivity*, Org. Lett. **24**, 35, 6417 – 6422 (2022). https://doi.org/10.1021/acs.orglett.2c02494
8. Yanbang Li, Rohin Biswas, William P. Kopcha, Thierry Dubroca, Laura Abella, Yue Sun, Ryan A. Crichton, Christopher Rathnam, Letao Yang, Yao-Wen Yeh, Krishnendu Kundu, Antonio Rodríguez-Fortea, Josep M. Poblet, Ki-Bum Lee, Stephen Hill, Jianyuan Zhang, *Structurally Defined Water-Soluble Metallofullerene Derivatives towards Biomedical Applications*, Angew. Chem. **62**, e202211704 (2023). https://doi.org/10.1002/anie.202211704

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Conference proceeding (retrievable through DOE PAGES):

- Application of wideband pulsed high-frequency EPR to molecular quantum spin science, Manoj Vinayaka Hanabe Subramanya, Elvin Salerno, Krishnendu Kundu, Jonathan Marbey, Johannes E. McKay and Stephen Hill, 73rd Yamada Conference, Sendai, Japan, October 8 – 11, 2022.

4. Human Resource Development

The project has provided extensive research opportunities to graduate student and postdoctoral research associates at Florida State University and Rutgers University. These personnel, which include 9 graduate students and 3 postdocs, have received cutting-edge training in the highly interdisciplinary and growing area of molecular quantum spin science. Two of the graduate students, Jonathan Marbey and William Kopcha, completed their studies during the project reporting period and have moved on to positions at government labs. Four more students are very close to completion of their PhDs. Two of the postdocs have moved on to full-time positions, one at a government lab and another in industry; the third has continued in the PI's group. All of the students and postdocs have received training in a wide range of synthetic and experimental skills.

The following activities stand out in terms of impact on the development of human resources:

1. Students and postdocs attended the following conferences, where they made presentations:

    - American Physical Society March Meeting, Las Vegas, March 5 – 10, 2023.
    - 50th Southeastern Magnetic Resonance Conference, Tallahassee, FL, Nov. 4 – 6, 2022.
    - 43rd EPR Symposium at the 61st Rocky Mountain Conference on Magnetic Resonance, Copper Mountain, CO, July 25 – 29, 2022.
    - Workshop at Telluride Science Research Center entitled "From Fundamentals of Molecular Spin Qubit Design to Molecule-Enabled Quantum Information", Telluride, Colorado, June 6 – 10, 2022.
    - 2nd Molecular Magnetism in North America (MAGNA 2022) conference, Gainesville, FL, May 1 – 4, 2022.
    - 88th Annual Meeting of the Southeastern Section of the American Physical Society, Florida State University, November 18 to 20 (2021).
    - 49th Southeastern Magnetic Resonance Conference, Louisiana State University, October 22 – 24, 2021.
    - Magnetism in North America (MAGNA) Conference, St. Simons Island, GA, Feb. 21 – 24, 2020.

2. The MagLab organizes a series of monthly professional development activities for postdocs and graduate students. These include seminars, e.g., how to prepare a CV, how to prepare for faculty positions, etc. Many of these activities have continued online during 2021/22.
3. All researchers at the MagLab are required to undergo extensive online safety training, with annual refreshers and regular lab-wide meetings devoted to safety. In addition, a separate COVID-19 safety training course was required for all MagLab personnel since the onset of the pandemic.

4. The MagLab organizes mandatory quarterly meetings for its staff and students, with each meeting focused on various news items and professional development topics. These meetings were originally focused on safety, but now deal with diverse topics such as diversity and how implicit bias can influence job searches. The meetings have continued online during the pandemic, and will likely remain so in order to reach a wider audience.
5. Members of the PI's group are able to attend a number of weekly seminars, both at the MagLab and across campus. These have been a mix of online and in-person during the 2021/22 academic year.

5. Development of Institutional Resources

1. The PI performed multiple service functions associated with the MagLab, including: responding to rapid calls for information from the lab leadership and the NSF; preparation of highlights and reports for the NSF; reviewing magnet time applications; and the day-to-day running of the EMR user program. The PI currently serves on the Search Committee for the next Director of the MagLab.
2. The PI is spearheading a truly multidisciplinary effort aimed at establishing a Quantum Science and Engineering Institute at Florida State University, involving faculty from 12 departments and three colleges. This effort will eventually result in the creation of new graduate and undergraduate degree programs in quantum information science. The FSU Upper Administration has announced strong support for this effort, with investments in the hiring of new faculty (currently ongoing), allocating space for the effort in a new Interdisciplinary Research and Commercialization building that is currently under construction, as well as startup costs for faculty and key infrastructure required to launch the initiative. See: https://news.fsu.edu/news/science-technology/2023/04/12/fsu-announces-bold-investments-in-quantum-science-and-engineering/.
3. The PI served on the National Academies of Science, Engineering and Medicine (NASEM) Committee on Exploring Opportunities at the Interface Between Chemistry and Quantum Information Science, sponsored by the National Science Foundation and the Department of Energy. The final report resulting from this effort is now available online at: https://nap.nationalacademies.org/read/26850/chapter/1.

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7. Disclaimer

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Department of Energy.