Summary: Nuclear magnetic resonance is a powerful tool to shed light on the properties of a vast range of materials but its use is affected by detection sensitivity. Throughout this work, we investigated new routes to dynamic nuclear spin polarization with an eye on applications to the study of metal-organic frameworks (MOFs). Work at the Meriles group focused on extending our understanding of the mechanisms governing the optical generation of spin order via photo-active electronic spin species and the subsequent transfer of spin polarization throughout the solid-state host.

FINAL TECHNICAL REPORT FOR AWARD DOE-BES-SC0020638

1. What are the major goals of the project?

This project articulates magnetic resonance and optical spectroscopy methods to investigate the spin dynamics of metal organic frameworks (MOFs), with special attention to using optical pumping schemes to improve detection sensitivity of nuclear spin polarization in MOFs as well as the development and application of new MOF structures to quantum information science.

There are three areas of work for this project: optical spin pumping and dynamic nuclear polarization in MOF structures comprising optically-activated paramagnetic linker molecules whose spin populations become highly athermal upon light absorption; optical absorption and relaxation processes by design at the metal atoms of MOFs through the use of rare- earth ions; optical nuclear pumping of imbibed gases and liquids within MOFs to address fundamental questions of structure and transport within MOFs.

This work was carried out in collaboration with Prof. J. Reimer's lab at the University of California at Berkeley. Work at the Meriles group (CUNY – City College of New York) focused on the investigation of the mechanisms underlying the transport of spin polarization in a solid matrix.

2. What was accomplished under these goals?

The bullet points below summarize the main activities:

- ***DNP mediated spectroscopy of electron-nuclear clusters:*** Paramagnetic centers and nuclear spins in a MOF are expected to group randomly and form clusters featuring nearly-degenerate, hybrid states whose dynamics is central to processes involving nuclear spin-lattice relaxation and diffusion. Their characterization, however, has proven notoriously difficult mostly due to their relative isolation and comparatively low concentration. We combined field-cycling experiments with variable radio-frequency (RF) excitation to probe the transitions of hybrid electronic-nuclear spin clusters. We experimentally investigated the regime of continuous optical and RF excitation to establish a connection between the steady state of the spin cluster and the observed polarization of bulk nuclei (which we exploited as a long-term memory). We uncovered complex nuclear polarization patterns of alternating sign that we qualitatively captured through analytical and numerical modeling. Our results unambiguously expose the impact that strongly-hyperfine-coupled nuclei can have on the spin dynamics of the solid as a whole, and inform future routes to spin cluster control and detection. The manuscript by Pigliapochi et al reports on these results (R. Pigliapochi, D. Pagliero, L. Buljubasich, P.R. Zangara, C.A. Meriles, *Phys. Rev. B* **107**, 214202 (2023)).
- ***Development of new microwave-free DNP protocols:*** Dynamic nuclear polarization (DNP) presently stands as the preferred strategy to translate optical pumping into enhanced sensitivity of nuclear magnetic resonance measurements, but its application relies on the use of high-frequency microwave to manipulate electron spins, an increasingly demanding task as the applied magnetic field grows. We investigated the dynamics of a system hosting a polarizing agent formed by two

distinct paramagnetic centers near a level anti-crossing. We theoretically showed that nuclear spins polarize efficiently under a cyclic protocol that combines alternating thermal jumps and radio-frequency pulses connecting hybrid states with opposite nuclear and electronic spin alignment. Central to this process is the difference between the spin-lattice relaxation times of either electron spin species, transiently driving the electronic spin bath out of equilibrium after each thermal jump. Without the need for microwave excitation, this route to enhanced nuclear polarization may prove convenient, particularly if the MOF polarizing agent is designed to feature electronic level anticrossings at high magnetic fields. These results led to a publication (C.A. Meriles, P.R. Zangara, *Phys. Rev. Lett.* 128, 037401 (2022).

- ***Fluctuation driven DNP under feedback control:*** A spin ensemble in thermal equilibrium continuously undergoes random fluctuations analogous to those observed in Brownian motion, a process known as spin noise. We investigated the dynamics of a system comprising a spin-1 paramagnetic center (typical of triplet states of optically excited organic MOF linkers) and a hyperfine-coupled spin-1/2 nucleus in the vicinity of a level crossing. We theoretically showed that nuclear spins polarize efficiently under the combined action of thermal fluctuations and a closed-loop feedback protocol. The latter articulates periodic observations of the electronic magnetization and radio-frequency pulses connecting hybrid states with opposite nuclear spin alignment. Since nuclear polarization emerges from electronic spin fluctuations, not spin order, this microwave-free technique generically benefits from warmer, not colder, operation temperatures. Further, because the spin dynamics at play near a level crossing is rather insensitive to the absolute value of the magnetic field, our work promises opportunities for high-field dynamic nuclear polarization, difficult to attain through present methods. A manuscript discussing these results was published in Phys. Rev. Applied (S. Bussandri, G. Sequeiros, R.H. Acosta, P.R. Zangara, C.A. Meriles, *Phys. Rev. Appl.* **18**, 034039 (2022)).
- ***Non-Hermitian dynamics of spin chains.*** Connected with the studies above, we found that the interplay between optical pumping and spin-lattice relaxation in molecular systems such as a MOF - hosting regular arrays of electron and nuclear spins - can lead to unanticipated, non-trivial dynamics. Focusing on periodic, one-dimensional chains, we theoretically showed that by adjusting the electron spin pumping to a critical level, it is possible to steer the flow of nuclear polarization to create site-dependent distributions where either end of the array polarizes in opposite ways, irrespective of the initial state. By contrast, we found that ring-like patterns — where the limit nuclear polarization is uniform — exhibit a non-decaying, externally-driven nuclear spin current. Interestingly, cyclic magnetic field modulation can render these processes largely robust to defects in the chain, a response featuring some interesting similarities — and differences — with recent findings in other non-Hermitian physical platforms. A research article reporting on these findings were published in *Physical Review B* (S. Bussandri, P.R. Zangara, R.H. Acosta, C.A. Meriles, *Phys. Rev. B* **103**, 214409 (2021)).
- ***Investigation of rare-earth emitters.*** Since the optical characterization of rare earth ions is central to our plans, we devoted a fraction of our effort to investigate how to best optimize photon collection from these emitters. Thanks to the screening of their partially filled 4*f* orbitals, rare-earth (RE) ions are found to exhibit atom-like optical transitions, often insensitive to the choice of the host matrix. A main consequence of their narrow optical linewidths, however, is that the fluorescence from RE emitters is intrinsically faint, hence complicating the isolation of individual ions and their spin manipulation. To overcome this limitation, we investigated the response of rare-earth emitters in Eu^{3+} $(NO_3)_3 6\text{-}H_2O$ nanoparticles overlaid on a metamaterial formed by a hexagonal array of Ag nanowires grown within a porous Al_2O_3 matrix. The metamaterial-coupled Eu^{3+} ions exhibit up to a 2.4-fold increase in their decay rate, accompanied by an enhancement of the emission rate from the $^5D_0 \rightarrow ^7F_2$ transition. To support these observations, we implemented finite-difference time-domain modeling and found an increase in the photonic density of states seen by the Eu^{3+} ions in the proximity of the metamaterial, consistent with experiment. These results led to a research article by G. Lopez et al. (G.I. López-Morales, M. Li, A. Hampel, S. Satapathy, N.V.

Proscia, H. Jayakumar, A. Lozovoi, D. Pagliero, G.E. Lopez, V.M. Menon, J. Flick, C.A. Meriles, *Opt. Mater. Exp.* **11**, 3478 (2021)).

3. What opportunities for training and professional development has the project provided?

The project provided partial support for a female postdoctoral scientist who has led the experimental activities at CUNY. Also associated with the project on the CUNY side was a masters student tasked with the development of a low-field variable temperature NMR setup. The Meriles group also hosted several REU students (10 in total), most of them belonging to under-represented groups.

4. How have the results been disseminated to communities of interest?

The bullet points below indicate some of the presentations by the Meriles group connected to this project:

- "Inductive detection and coherent control of electronic-nuclear multi-spin clusters", APS March Meeting, Mar 2022
- "Microwave-free dynamic nuclear polarization via sudden thermal jumps", Eastern Analytical Symposium, Nov 2021
- *"Exploiting Landau-Zener Crossings from Athermal Electrons for Nuclear Hyperpolarization,"* Invited Lecture 2021 International Society for Magnetic Resonance Conference, August 23, 2021.
- "Spontaneous emission dynamics of Eu^{3+} ions coupled to hyperbolic metamaterials", *APS March Meeting*, March 2021.
- "One-directional transport of spin polarization in electron/nuclear spin chains with loss and gain", *APS March Meeting*, March 2021
- "One-directional transport of spin polarization in electron/nuclear spin chains with loss and gain", *ENC Conference,* March 2021.