DOE BES Final Technical Report

1. DOE Award # and Name of the Recipient (Institution)

DOE Award #:

DE-SC0023433

Name of the Recipient:

University at Buffalo, The State University of New York

2. Project Title and Name of the PI

Project Title:

"Molecular Heterogeneous Multiferroics"

Name of the PI:

Dr. Shenqiang Ren (University at Buffalo, The State University of New York), PI

3. Date of the report and research period covered by the report

Date of the Report:

8/15/2023

Research Period Covered by the Report:

08/15/2022 ~ 08/15/2023

4. Program Manager

Dr. Ahmet Refik Kortan

A. Executive Summary

This project aims to explore a new class of molecular heterogeneous multiferroics towards room temperature stimuli-responsive magnetoelectricity by untangling the complex interplay between molecular magnetism and molecular ferroelectricity, and their stimuli-responsiveness. The research hypothesis is to examine if the rational design and molecular engineering of hydrogen bonded molecular heterogeneous multiferroics will enable rapid proton-transfer between molecular ferroelectric and magnetic building blocks to control its magnetism and intramolecular spin and dipole interactions, a promising pathway toward a new mechanism of room temperature ME coupling effect in molecular materials. With arbitrary choice and precise organization of molecular building blocks underlying tunable spin and dipole interactions, driven by external stimuli (electrical, magnetic and optical), a variety of multifunctional molecular multiferroics will be created and characterized, which could provide the understanding for the design of next-generation stimuli-responsive molecular magnetoelectronics.

The PI seeks to explore the discovery of room temperature molecular heterogeneous multiferroics, and the fundamental and mechanistic understanding of multiferroicity of molecular solids. The experimental results have been complementary evaluated and corroborated through the computational modeling. Some **key findings** are observed in the Year-1 as following:

- Chemical engineering tailors superconducting 2D FeSe materials to accelerate superconducting materials discovery. Solid state reaction after the controlled growth of FeSe thin films is demonstrated by the chemical engineering to create heterogenous interface in FeSe films via a solution-based environment. The two-step route allows an expanded crystal structure and enhanced superconducting transition temperature from 3.6 to 38 K, providing a new strategy to design functional hybrid materials.
- The 2D molecular magnets provoke a surge of interest in large anisotropy in reduced dimensions and are promising for next-generation information technology where dynamic magnetic tuning is essential. We demonstrate an in-situ chemical tuning route to control transformation of low-temperature magnetic order into room-temperature molecular hard magnetism. The chemical tuning via electrochemical lithiation and solvation/desolvation exhibits continuously variable magnetic features from cryogenic magnetism to the room-temperature optimum performance of coercivity (Hc) of 8500 Oe and energy product of 0.6 MGOe. Such chemically flexible tunability of room-temperature magnetism is ascribed to the different degrees of lithiation and solvation that modify the stoichiometry and Cr-pyrazine coordination framework. The findings here suggest chemical tuning as a universal approach to control the anisotropy and magnetism of 2D hybrid magnets at room temperature, promising for data storage, magnetic refrigeration, and spintronics.

Impact of Findings:

The recently discovered two-dimensional (2D) magnets constitute an ideal platform to access fundamental physics of magnetism in reduced dimensions, on which it has been fueling interests in exploring atomically thin and flexible magnetoelectric devices allowing electrical control and chemical functionalization. However, a long-standing missing member in the family of 2D magnets is 2D molecular hard magnets that exhibit large magnetic anisotropy and operate above room temperature. We present two-dimensional $Cr(pyz)_2 \cdot xLiCl \cdot yTHF$ (LCPC) molecular hybrid magnet, exhibiting magnetic ordering above 510 K, unprecedented high saturation magnetization of 28 emu/g and coercivity of 8500 Oe (Fig. 1). An in-situ electrochemical route is demonstrated to realize controllable coordination frameworks of 2D LCPC by transforming the octahedral coordination of Cr

into 2D coplanar Cr-pyrazine layered framework, which is indispensable to dynamically tune magnetic energy product that relates to magnetic anisotropy and saturation magnetization. In addition, by varying the stoichiometry, we observe the anisotropy transitions between magnetically soft and hard phases due to the dynamic tuning of exchange interactions. Meanwhile, additively manufactured 2D magnets allow excellent air stability and strong electromagnetic induction, prerequisite for the development of practical applications. In addition, several high-impact journal articles are published in the one-year project. Below we report all of these.

B. DOE-Supported Publications

1. Yulong Huang*, Jennifer L. Gottfried, Arpita Sarkar, Gengyi Zhang, Haiqing Lin, Shenqiang Ren*, Proton-controlled Molecular Ionic Ferroelectrics, Nature Communications, 2023, 10.1038/s41467-023-40825-6. **Acknowledgment:** The U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering supports S.R. under Award DE-SC0023433.

2. Yulong Huang*, Arjun K. Pathak*, Jeng-Yuan Tsai, Clayton Rumsey, Mathew Ivill, Noah Kramer, Yong Hu, Martin Trebbin, Qimin Yan* & Shenqiang Ren*, Pressure-controlled magnetism in 2D molecular layers. Nature Communications, 2023, 14(1), 3186. **Acknowledgment:** The U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering supports S.R. under Award DE-SC0023433. The work at Buffalo State was supported by the National Science Foundation Award No. DMR-2213412. J.Y.T. and Q.M.Y. are supported by the National Science Foundation under Grant No. 2144936.

3. Yulong Huang,* and Shenqiang Ren*, Controlled growth and chemical engineering of FeSe-based superconducting films, Advanced Physics Research, 2022, 2(4), 2200058. **Acknowledgment:** The authors indeed thank Prof. David B. Eason for his contribution on FeSe film growth in this work that is in memory of him. The U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering supports S.R. under Award DE-SC0023433.

4. Yulong Huang, Qiang Zhang, Yuguang C. Li, Yu Yao, Yong Hu, Shenqiang Ren*, Chemical tuning Meets Two-Dimensional Molecular Magnets, Advanced Materials, 2022, 35(5), 2208919. **Acknowledgment:** The U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering supports S.R. under Award DE-SC0023433.

C. People

1. Dr. Yulong Huang, Postdoctoral Associate, 100 % from this project