

## Metal-Organic Organic Frameworks: A New Class of Non-Pb-based Multiferroics for Simultaneous Electrically and Magnetically Controlled Quantum Memories

Aided by recent advancements in the field of hybrid inorganic-organic frameworks, or MOFs, my research at Florida State began with an aim to synthesize a hybrid counterpart of magnetic-core memory. Magnetic-core memory was the predominant form of random-access computer memory for 20 years, from 1955-75. MOFs are hybrid crystalline materials comprised of inorganic and organic building blocks, as illustrated in figure 1.1. By varying both the building blocks and the synthesis conditions, an infinite number of such novel materials could be synthesized.

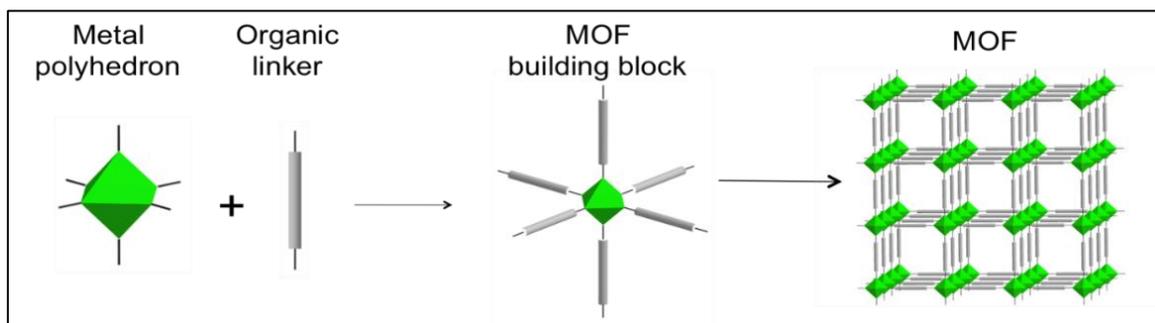


Figure 1.1: Prototypical MOF structure made up of a periodic arrangement of inorganic (metal) and organic components

We (my then graduate student Prashant Jain, Prof. Naresh Dalal, and Prof. Tony Cheetham) began our research with the aim of creating a planar 2-D MOF materials to mimic iron-core memory. However, serendipitously, we synthesized a perovskite MOF which was disordered at the room temperature. Perovskite materials generally exhibit many interesting and intriguing properties: colossal magnetoresistance, ferroelectricity, superconductivity, charge ordering, spin dependent transport, high thermopower and the interplay of structural, magnetic and transport properties are commonly observed. Thus, this exciting discovery of hybrid perovskites led us to research Pb-free ferroelectrics and a new class of multiferroic materials which is detailed below:

### 1.1 Ferroic ordering in a metal-organic-framework (MOF)

{1. *Journal of the Americal Chemical Society* 130 (32):10450-10451; 2. *Proceedings of the National Academy of Sciences* 108 (17):6828-6832.}

#### ***Journal of the Americal Chemical Society* 130 (32):10450-10451, 2008**

Our research interest in MOFs sprang from their potential in condensed matter physics applications, especially their hybrid nature, which provided the opportunity to realize properties otherwise not possible in a single component pure organic or inorganic system. Prior to this work, ferroelectric ordering transition in the porous MOFs  $[\text{Mn}_3(\text{HCOO})_6](\text{H}_2\text{O})(\text{CH}_3\text{OH})$  and  $[\text{Mn}_3(\text{HCOO})_6](\text{C}_2\text{H}_5\text{OH})$  had been reported. In these works, methanol ( $\text{CH}_3\text{OH}$ ) and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) were loosely bound guest molecules in the pores, and ordering of these molecules results in net polarization. However, due to the low boiling points of these guest molecules, they tend to escape at room temperature, rendering

the ferroelectric properties hard to reproduce for practical applications. In order to solve this problem, we investigated hybrid perovskite  $[(\text{CH}_3)_2\text{NH}_2]\text{Zn}(\text{HCOO})_3$  (DMA-Zn-F: dimethylammonium-zinc-format) (see structure in Figure 1.2 where the guest molecule  $[(\text{CH}_3)_2\text{NH}_2]^+$ , dimethylammonium cation, is an integral part of the crystal structure and cannot escape the cubic cage formed by  $\text{Zn}(\text{HCOO})_3$ . Additionally, the guest molecule was hydrogen bonded to the cubic cage, making it disordered at room temperature. We showed that, on lowering the temperature, dimethylammonium cation becomes ordered, rendering the compound ferroelectrically ordered. We used synchrotron x-ray diffraction, dielectric constant, and heat capacity measurements to show that this unique order-disorder type ordering occurs at a relatively convenient temperature of 156 K. This material also falls into the category of high dielectric constant material with a dielectric constant of 15. This type of electrical ordering associated with an order-disorder phase transition was unprecedented in hybrid frameworks/MOFs and opened up an exciting, new direction in rational synthetic strategies to create extended hybrid networks for applications in ferroic-related fields.

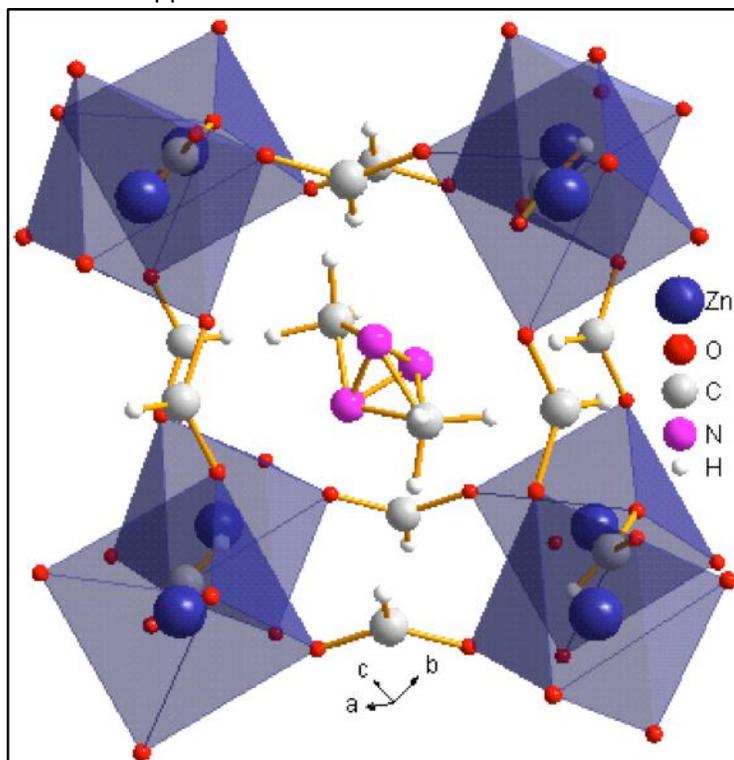


Figure 1.2 Crystal structure of  $[(\text{CH}_3)_2\text{NH}_2]\text{Zn}(\text{HCOO})_3$  at room temperature. It has the same architecture as an  $\text{ABX}_3$  perovskite, with  $\text{A}=(\text{CH}_3)_2\text{NH}_2^+$  (DMA),  $\text{B}=\text{Zn}^{2+}$ , and  $\text{X}=\text{HCOO}$ . The purple spheres represent the three dynamically disordered sites for the N atom of the DMA cation.

***Proceedings of the National Academy of Sciences* 108 (17):6828-6832, 2011**

In the second part of this project, using detailed NMR and specific heat ( $C_p$ ) measurements on DMAZnF, we demonstrated (i) a slowing down of the hopping motion of the caged dimethylammonium moiety, with a minimum in the  $1\text{H}$  spin-lattice relaxation time ( $T_1$ ) around the phase transition; (ii) an unusual memory effect in the temperature dependence of  $T_1$  at temperatures below the phase transition, implying glass-like behavior; and (iii) a peak in  $C_p/T^3$  vs.  $T$  data, which corroborates the presence of a glassy phase, which is more common in inorganic perovskite materials. This was the first report of glassy behavior in a MOF.

## 1.2 Multiferroic metal-organic-frameworks (MOF)

{3. *Journal of the American Chemical Society* 131 (38):13625-13627, 2009; 4. *Physical Review B* 82 (1), 2010; 5. *Dalton Trans* 41 (14):3949-3952, 2012.}

Multiferroics are attractive candidates for use in electrically controllable microwave elements, magnetic-field sensors, and possibly even in spintronics. Recent years have, therefore, seen a considerable worldwide effort to discover broad classes of multiferroics, using a combination of materials chemistry, theoretical approaches, and synthetic techniques. Unfortunately, it is becoming increasingly clear that the electronic structures of molecules that are required for ferromagnetism and ferroelectricity tend to be mutually exclusive. Ferromagnetism typically requires unpaired electrons that interact through a quantum-mechanical process known as exchange coupling. But typical ferroelectric materials (such as barium titanate, BaTiO<sub>3</sub>, and other structurally related 'perovskite' compounds that contain transition metals) require the transition-metal ion to have an empty outer shell of electrons. This fundamental contrast is the chief reason few materials are both ferroelectric and ferromagnetic.

Most researchers have adopted four main approaches -- lone-pair effect, geometric frustration, charge ordering, and magnetic ordering -- to create magnetoelectric materials. All of these attempt to introduce ferroelectricity into magnetic materials, engaging various mechanisms to sidestep the fundamental mismatch described above.

### ***Journal of the American Chemical Society* 131 (38):13625-13627, 2009**

In the case of DMAZnF, the origin of the electric ordering is intrinsic, and moreover, not dependent on solvent contents. And, in this project, we successfully replaced non-magnetic zinc ions with magnetic Mn, Co, Ni, and, Fe ions while keeping the perovskite structure of DMAZnF intact. We demonstrated that electrical ordering was also present in these new materials. These magnetic analogues showed ferromagnetic ordering below 8.5K to 35.6K, depending upon the transition metal ion. Electric ordering was also tunable and varied from 160-185K, as a function of transition metal ions. Below the magnetic ordering temperature, electrical ordering co-exists with magnetic ordering, thus making these materials the first series of multiferroic MOFs (Figure 1.3). We employed a number of advanced techniques, including, synchrotron radiation, single crystal x-ray diffraction, heat capacity, dielectric constant measurements, magnetic susceptibility measurements, and electron paramagnetic resonance to study various properties of these MOFs.

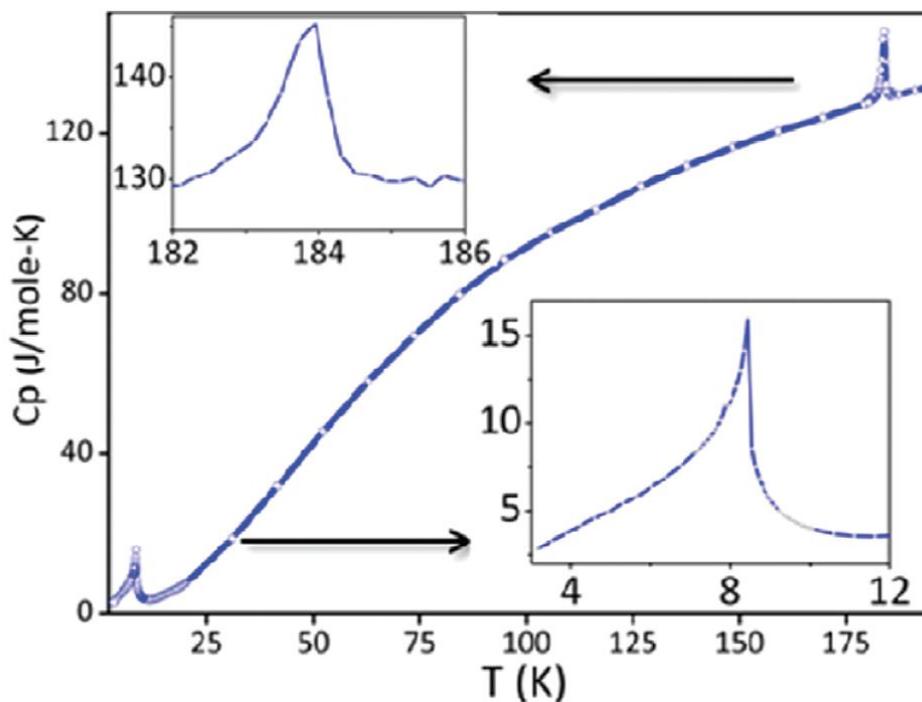


Figure 1.3: Heat capacity of DMAMnF as a function of temperature. The anomalies relating to electrical ordering and magnetic ordering are clearly seen at 184 and 8.4 K.

***Physical Review B 82 (1), 2010***

In the next part of this project we studied the magnetic properties of these multiferroic MOFs using muon spin relaxation technique. Muon spin spectroscopy is based on the implantation of spin-polarized muons in matter and on the detection of the influence of the atomic, molecular or crystalline surroundings on their spin motion. The motion of the muon spin is due to the magnetic field experienced by the particle and provides information on its local environment in a very similar way to other magnetic resonance techniques, such as electron spin resonance (ESR or EPR) and, more closely, nuclear magnetic resonance (NMR). We used muons to follow the sublattice magnetization, observing the effect of the spin reorientation transitions below the magnetic ordering temperature and the criticality approaching it. Using the data, we modeled the magnetic structure of multiferroic MOFs and showed that they have three dimensional antiferromagnetic interactions. In addition, the copper analogue demonstrated quasi-one-dimensional behavior due to its Jahn-Teller distorted structure. Muon data on these samples allowed us to track the sublattice magnetization rather than the bulk magnetization due to the weak ferromagnetism that is seen in magnetic susceptibility measurements.

***Dalton Trans 41 (14):3949-3952, 2012***

In this work, we studied the elastic properties of DMAMF (M=Zn, Co, Ni, Mn) single crystals by means of nanoindentation. Nanoindentation is a variety of indentation hardness tests applied to small volumes. Indentation is, perhaps, the most commonly applied means of testing the mechanical properties of materials. Unlike typical open-framework MOFs, there is no solvent accessible volume present within DMAMF. As such, DMAMF is deemed to be structurally more robust, not only because

the hybrid framework is essentially dense, but also the nature of its electrical ordering is intrinsic to the parent structure and thereby independent of extra guest molecules. Basic information about their structural stability when subjected to mechanical stresses is crucial to any practical applications. We synthesized high quality single crystals, which presented us with an interesting opportunity to compare the Young's moduli ( $E$ ) of four isostructural DMMF materials that differ only in terms of their transition metal cations, of which  $M = \text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$ . We obtained the unexpected results that the elastic moduli of isostructural DMAMF compounds are not straightforwardly correlated to the cation radius, but instead can be explained by accounting for their ligand field stabilization energy. We demonstrate that the  $\text{Ni}^{2+}$  structure exhibits the greatest mechanical stability (in elastic domain) by virtue of its strongest ligand field stabilization. Our findings provided the fundamental understanding required for future investigations focusing on: (a) the effects of temperature and phase transitions on the mechanical response, (b) direct measurements of the elastic stiffness tensor ( $C_{ij}$ 's) for establishing the shear and bulk moduli and Poisson's ratio, (c) elastic–plastic transition by means of spherical nanoindentation, and (d) determination of fracture characteristics.

### 1.3 Multiferroic materials with magnetoelectric coupling

{6. *Physical Review B (Condensed Matter and Materials Physics)* 87 (22):224406–224408, 2013; 7. *Physical Review B* 86 (21), 2010; 8. *Acta Materialia* 61 (13):4928–4938, 2013; 9. *Angew Chem Int Ed Engl* 50 (26):5847–5850, 2011.}

To date, multiferroics, both in bulk and heterostructure form (where two separate materials are combined to achieve the combination of ferroelectric and ferromagnetic properties), are still struggling to achieve sufficient magneto-electric coupling for practical use. This coupling is not automatic because ferromagnetism and ferroelectricity break different symmetries (time reversal and spatial-inversion, respectively). Because of this requirement of breaking of different symmetries, much research is focused on hetero-structures of ferromagnetic and ferroelectric materials in order to achieve magnetoelectric coupling. In multiferroic thin films, the coupled magnetic and ferroelectric order parameters can be exploited for developing magnetoelectronic devices. These include novel spintronic devices, such as tunnel magnetoresistance (TMR) sensors and spin valves with electric field tunable functions. A typical TMR device consists of two layers of ferromagnetic materials separated by a thin tunnel barrier ( $\sim 2$  nm) comprised of a multiferroic thin film. In such a device, spin transport across the barrier can be electrically tuned. In another configuration, a multiferroic layer can be employed as the exchange bias pinning layer. If the antiferromagnetic spin orientations in the multiferroic pinning layer can be electrically tuned, then the magnetoresistance of the device can be controlled by the applied electric field. One can further explore multiple state memory elements, where data is stored both in the electric and the magnetic polarizations. Plainly, efficient multiferroic materials hold great potential for technological advances.

After demonstrating that it is possible to have both magnetism and ferroelectricity in a new class of materials, we focused on the cross coupling of these two phenomena where ferroelectric order parameter, electric polarization can be controlled by magnetic field and vice versa. This allows for the possibility of previously mentioned multiple state memory elements, where data is stored both in the electric and the magnetic polarizations. Further, there is particular need for magneto-dielectrics in real world applications, e.g. miniaturized broad-band antennas in high-flying aircraft and satellites.

Moreover, there are opportunities to realize novel functional behavior in multiferroics by coupling lattice strain to magnetic and/or electric properties (Figure 1.4). In the research described below, we showed that MOFs are an excellent choice of materials to couple elastic properties to other multiferroic properties of materials.

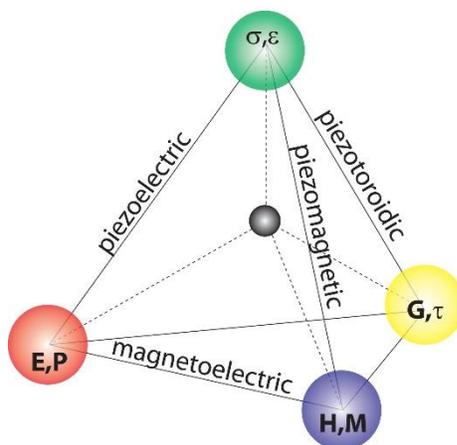


Figure 1.4: Opportunities to realize novel functional behavior in multiferroics.

***Physical Review B* 86 (21), 2010**

In this project, we used resonant ultrasound spectroscopy to analyze magnetic and ferroelectric phase transitions in two multiferroic metal-organic frameworks (MOFs):  $(\text{CH}_3)_2\text{NH}_2\text{M}(\text{HCOO})_3$  (DMA[M]F,  $\text{M} = \text{Co}^{2+}, \text{Mn}^{2+}$ ). Resonant ultrasound spectroscopy (RUS) is used for measuring fundamental material properties involving elasticity. This technique relies on the fact that solid objects have natural frequencies at which they vibrate when mechanically excited. With the help of RUS, we discovered that elastic and anelastic anomalies are evident at both the magnetic ordering temperature and above the higher temperature ferroelectric transition. Broadening of peaks above the ferroelectric transition implies the diminishing presence of a dynamic process and is caused by an ordering of the central DMA cation, which ultimately causes a change in the hydrogen bond conformation and provided the driving mechanism for ferroelectricity. Elastic stiffening at low temperatures suggests weak magnetoelastic coupling in these materials. This is the first evidence of magnetoelastic coupling in MOFs and could help lead to the tailoring of MOFs with a larger coupling leading to magnetoelectric coupling via a common strain mechanism.

***Acta Materialia* 61 (13):4928-4938, 2013**

In our endeavor of exploiting perovskite MOFs for multiferroic properties, we discovered a first order ferroelastic phase transition in orthorhombic  $Pnma$  to monoclinic  $P2_1/n$  transition at  $\sim 272$  K in the hybrid perovskite,  $[(\text{CH}_2)_3\text{NH}_2][\text{Mn}(\text{HCOO})_3]$  (azetidium-manganese-formate). Equivalent transitions do not occur in conventional inorganic perovskites, and we believe that this is the first example of improper ferroelastic behavior in a metal-organic framework with the perovskite structure. Detailed analysis of structure and symmetry indicate that the ferroelasticity is induced by order-disorder of the azetidium cations located in the perovskite cavities and associated changes in hydrogen bonding. Strain analysis shows

that linear strains of  $e_1$ ,  $e_2$  and  $e_3$  occur up to  $\sim 2\%$  at 120 K, and the shear strain  $e_5$  reaches  $\sim 5\%$ . Ferroelastic shear strains of this magnitude do not occur by octahedral tilting in conventional oxide perovskite materials, but they are comparable with shear strains due to cooperative Jahn–Teller distortions. This reflects the capacity of the highly flexible MOFs to relax in response to local changes in structure and probably, too, of the importance of hydrogen bonding in determining their ferroic properties.

***Angew Chem Int Ed Engl* 50 (26):5847-5850, 2011**

Using computational tools we showed that a recently synthesized MOF,  $C(NH_2)_3Cu(HCOO)_3$  (Cu-MOF), could be interesting from the multiferroic perspective. It has a polar space group required for ferroelectricity and it was shown to exhibit spin-canted antiferromagnetism with a Neel temperature of 4.6K. Only copper (Cu) analogue of this series of MOFs showed a polar structure due the Jahn-Teller-active  $Cu^{2+}$  ions. Our study showed that this Cu-MOF should be a new multiferroic metal–organic framework, in which the Jahn–Teller and antiferro-distortions cooperate to induce a switchable ferroelectric polarization by coupling to the A-group atoms through hydrogen bonding. Most importantly, a weak ferromagnetic component is coupled to the spontaneous polarization, and they are mutually reversible. Thus, our results show that Cu-MOF should exhibit weak ferromagnetism coupled with ferroelectricity, a rare phenomenon, making it a true magnetoelectric multiferroic.

Our work in news:

G. Rogez, N. Viart and M. Drillon. Multiferroic materials: the attractive approach of metal–organic frameworks (MOFs). **Angew. Chem. Int. Ed.** 2010, 49, 1921 – 1923. (Highlight)

High-Tech Applications Envisioned for Multiferroic Crystals. **ScienceDaily**, Feb 13, 2010.

Materials chemistry: Marvellous Metal–Organics. **Nature**, Vol 462, 24, 31 December 2009 (Research highlights)

R. Ramesh. Emerging Routes to Multiferroics. **Nature**, Vol 461, 29 October 2009 (News & Views)

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