Magneto-electric Coupling in a Metal-Organic Framework (MOF)

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Introduction: MOFs are hybrid materials made up of a long range periodic arrangement of inorganic and organic building blocks. They are nanoporous materials often showing huge surface area which makes them a suitable candidate for H_2 storage, CO_2 capture, and gas separation. However, they also show interesting condensed matter physics properties. Multiferroics are rare materials with simultaneous ferroelectric and ferromagnetic ordering. We have shown that unlike oxides where the two mechanisms responsible for aforementioned properties works against one another, multiferroics could be realized in hybrid inorganic-organic systems. However, the holy grail from the technological perspective remains the realization of magneto-electric coupling. Below we show our exploratory work on a **m**ixed valence **i**ron **f**ormate framework (MIF-1), $Fe^{II}Fe^{III}(CH_3)_2NH_2(HCOO)_6$, that such a phenomenon could indeed exist in these systems.

Experimental: *Synthesis*: Large crystals of *MIF-1* were synthesized from a modified method adopted from the literature[1,2]. In a typical reaction, $Fe(NO_3)_3.nH_2O$ was heated with water and Dimethylformamide at 140 deg C for up to 3 days resulting into mm size black crystals.
Measurements: Magnetic measurements were done on a polycrystalline as well as single crystal samples of MIF-1. For dielectric measurements, various contact methods were tried including silver paste contacts as well as direct deposition of platinum. Measurements were carried out along various crystallographic axes. While this work was in progress another work on the material was appeared in JACS[3].

Results

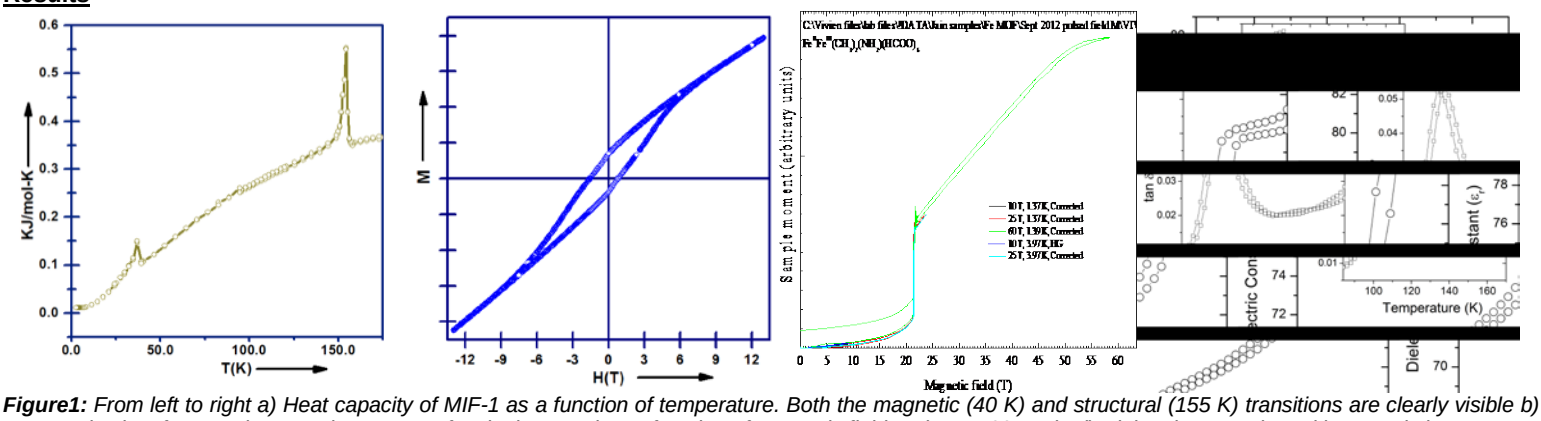

Figure1: *From left to right a) Heat capacity of MIF-1 as a function of temperature. Both the magnetic (40 K) and structural (155 K) transitions are clearly visible b) Hysteresis plot of MIF-1 c) Magnetic moment of a single crystal as a function of magnetic field and up to 60 Tesla d) Dielectric anomaly and hysteresis loop*

The structural transition is a result of ordering of the organic part in MIF-1 which also leads to a dielectric anomaly. An asymmetric hysteresis loop was observed for MIF-1 (Figure 1(b)). This phenomenon is known as the Exchange Bias and it refers to a shift of the ferromagnetic hysteresis loop along the field axis by an exchange bias field. It is of great interest due to its elusive microscopic origin and wide technological applications in high-density magnetic recording media, magnetic nonvolatile memories, and spin valve devices. Further, not observed in previous report, a spin flop was also discovered in MIF-1 (Figure 1(c)). As expected, anomaly in the specific heat was accompanied by an anomaly in the dielectric constant at 155 K (Figure 1(d)).

Moreover, MIF-1 shows magnetodielectric effect close to room temperature. However the origin of this behavior remains unknown at present and need further exploring.

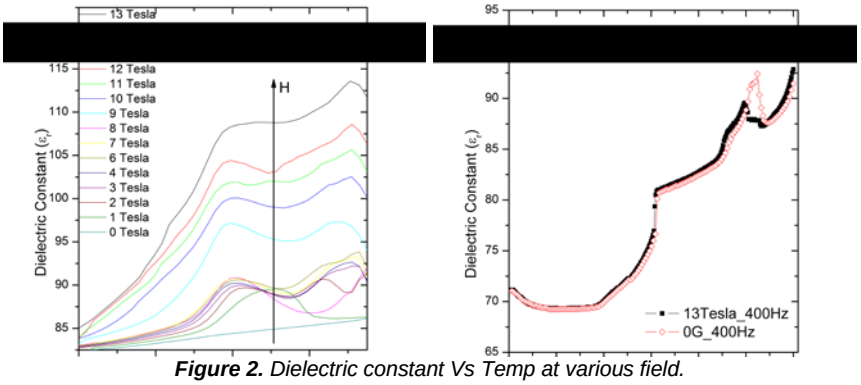

Figure 2. *Dielectric constant Vs Temp at various field.*

Conclusions: In conclusion, in our quest to discover new magnetoelectric materials, we have studied a mixed valence iron formate framework using various magnet lab facilities. The compound is made up of iron cations connected to each another by an organic formate linker. Pores of this nanoporous materials are occupied by dimethylammonium cation which is disordered at room temperature. On cooling MIF-1 goes under a ferroelectric phase transition at about 155 K. MIF-1 orders magnetically at 40 K. We also discovered that MIF-1 under goes a clear spin-flop transition at 14 Tesla. MIF-1 also shows magneto-dielectric coupling whose origin remains unknown and will need further exploration.

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References:

1. Inorganic Chemistry, Vol. 49, No. 22, 2010
2. J. Am. Chem. Soc., **2009**, 131 (22), 7516–7517
3. J. Am. Chem. Soc., **2012**, 134 (48), 19772–19781