

A porous crystal's penchant for bitter almonds

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The coupling of a change in bulk magnetism with emergent structural polarization can lead to a material exhibiting multiferroicity. In this preview, we highlight an excellent example of such a phenomenon, whereby a multiferroic metal-organic framework (MOF) features complex chemical properties unlocked by... bitter almonds?

One of the tenets of the metal-organic framework (MOF) field has long been the ability to reversibly absorb guests. For the most part, these guests have been thought to interact via either chemisorption (i.e., the formation of a chemical bond to the scaffold) or physisorption (i.e., adhesion via quadrupolar and higher order multipolar interactions).¹ While the former can impact the local spin configurations of open-metal sites within the MOF, the guest in the latter is generally thought to play a lesser role in affecting the electronic properties of the bulk material. But what if the MOF were to dynamically restructure both its geometry and electronics upon the uptake of a physisorbed guest? Such systems would become particularly interesting when the emergent properties result in a difference in net polarization—perhaps accessed by a change in crystal symmetry—in addition to a change in local electronic spin configuration. In such cases, the MOF reveals itself as a multiferroic.²

Multiferroicity is notoriously difficult to predict from static crystal structures, but a few key compositional features point us in the right direction: the inclusion of spin-polarized metals (even if the structural ground state is spin-paired) and highly symmetric but structurally dynamic crystal systems.³ In such cases, multiferroic behavior is then accessed by a structural transition that changes the underlying crystal symmetry, coupled with a reorganization of electronic spin; in effect, accessing properties hidden from equilibrium

crystallography.⁴ Hence, in order for a MOF to be truly multiferroic the crystal should demonstrate an ordered-to-ordered structural transition, with a corresponding ordered-to-ordered spin transition. Such reports are exceedingly rare in the MOF field because polymorphism is difficult to observe⁵ (and also because we probably didn't know to look for these properties).

In this preview, we highlight a particularly compelling example of a multiferroic MOF, appearing in *Physical Review B*.⁶ There, Mariette and colleagues report on a low temperature, low-spin Fe²⁺ containing MOF ([Fe(tpv)₂(NCS)₂], Figure 1) that undergoes structural and spin-cross-over transitions as long as the pores are filled of benzaldehyde (incidentally, a compound smells of bitter almond, and also shows up in roasted coffee beans⁷). The authors show that not only does the MOF uptake the guest, but the benzaldehyde leads to a reduction in overall symmetry of the scaffold (in effect increasing material polarization) and a temperature-dependent spin-crossover; an elegant example of hidden multiferroicity.

At first glance, one might think that benzaldehyde is paramount to this process. While it undoubtedly promotes the phase transition, perhaps stabilizing the framework by dielectric screening,⁸ it is not clear that there is anything particularly unique about the benzaldehyde itself besides possessing a dipole moment to polarize the MOF. Instead, one should direct their focus to the highly provocative

finding that reduced symmetry seemingly alleviates the entropic propensity for the Fe²⁺ centers to remain high-spin (a spin-configuration, which itself is already quite unusual). The high-to-low spin transition for octahedral Fe²⁺ causes a significant local coordination environment change (Figure 1). Yet, the material does not appear to rigidly transition from high-to-low spin, instead showing complex dependency on temperature, i.e., the phase diagram is more than two-dimensional.

Generally speaking, high-spin configurations are entropically favored (and hence why we typically see high-spin at high-temperature). At the same time, a reduction in crystal symmetry may also be a source of increased entropy.⁹ Thus, materials featuring high-spin atoms in highly symmetrical crystal systems are only one unique point on an undoubtedly interesting potential energy surface; the manifestation of which can be monitored by temperature-dependent vibrational analysis. In this case, a closer examination of the vibrational modes associated with the Fe-N revealed that, with heating, the Fe-N stretching frequencies reduce in magnitude and shift in frequency as the material approaches the spin-transition. Such observations are a smoking gun for a phase transition and are sometimes called "soft modes".¹⁰ One may intuit that this aligns with progress toward a bond-breaking event (i.e., elongation of bonds in an anharmonic potential well), but the key difference here is the isolation of yet another ordered chemical structure, rather than a melted material.

Thinking more broadly about these phenomena, Mariette's work points to a subtle and compelling advance in MOF chemistry—coupling two physical

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<https://doi.org/10.1016/j.matt.2021.06.039>



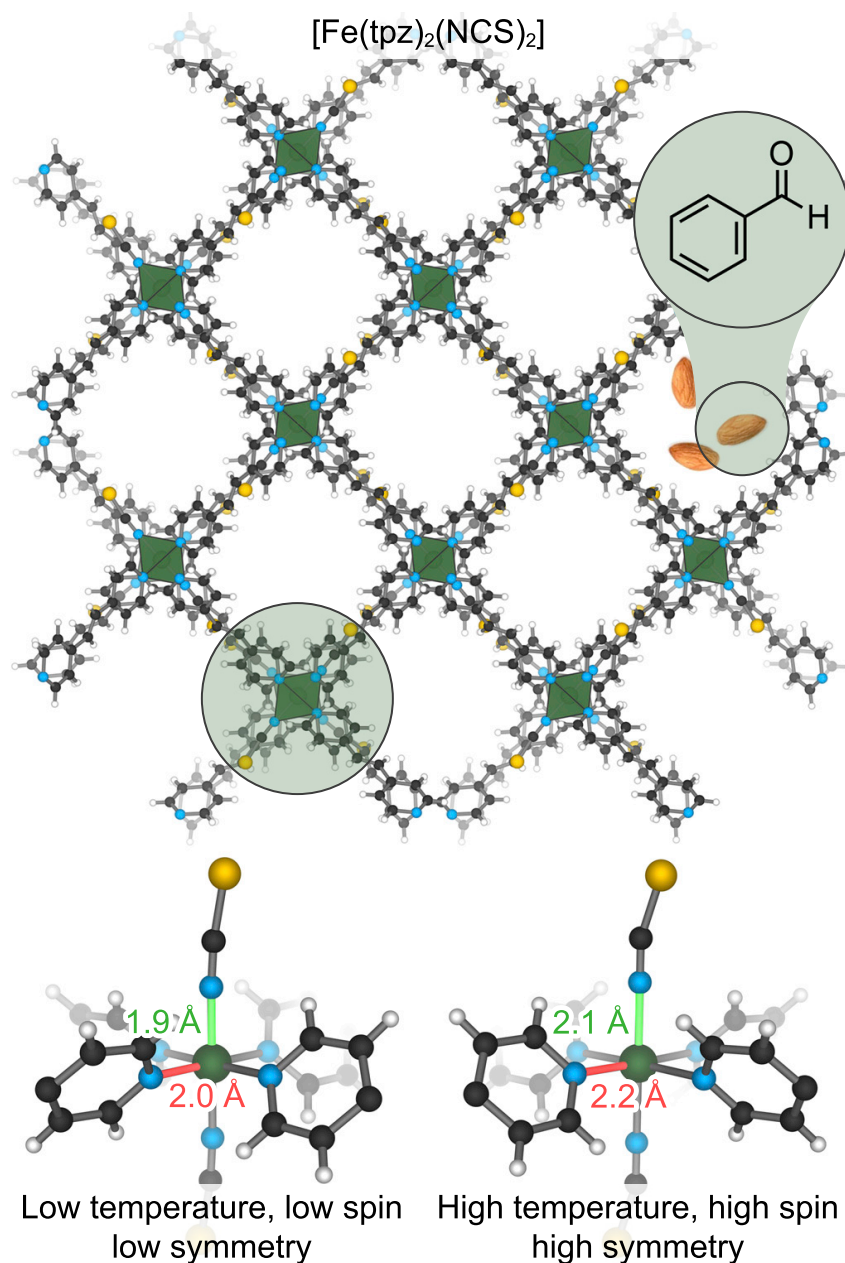


Figure 1. A Fe-based MOF with complex magnetic and polarization properties

The low temperature crystal structure of the Fe^{2+} -based spin crossover MOF undergoes significant structure reorganization upon heating in the presence of benzaldehyde.

properties (in this case structural ordering and local electronic spin ordering) to access chemistry that may not be obvious from a static crystal structure. In order to harness these properties, we need to get a handle on entropy. It is certainly difficult to predict which entropic driving force is larger (the entropy of having high symmetry versus local disorder, or

stronger metal-ligand bonds versus high-spin metal configurations).

At minimum, Mariette and colleagues have provided a compelling example of numerous pertinent phenomena in MOFs, and also comprehensive experimental roadmap for discovering multiferroicity in comparable systems. Such

studies highlight the value of entropy in ordered materials, potentially leading to multifunctional frameworks with multiferroic responses. Time will reveal how useful this will be, but we are delighted to see this result because it combines essentially all of the novel electronic and geometric properties that make MOFs special...alongside the tasty smell of benzaldehyde.

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