

PHYSICAL SCIENCES/MATERIALS SCIENCE/CONDENSED-MATTER PHYSICS/FERROELECTRICS AND MULTIFERROICS [/639/301/119/996]

PHYSICAL SCIENCES/CHEMISTRY/MATERIALS CHEMISTRY/METAL-ORGANIC FRAMEWORKS [/639/638/298/921]

PHYSICAL SCIENCES/MATERIALS SCIENCE/MATERIALS FOR ENERGY AND CATALYSIS/POROUS MATERIALS [/639/301/299/1013]

METAL-ORGANIC FERROELECTRICS

Polarisation from Sliding Molecular Rotors

The direct manipulation of a new kind of ferroelectric state, arising from the sliding of van der Waals layers in a coordination polymer, is demonstrated.

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Developing novel ferroelectrics that can find applications as switches, sensors and storage bits presents a substantial design challenge. Conventional ceramic devices have traditionally relied on perovskite-based materials containing ions such as lead or titanium that prefer off-centre coordination environments on account of their specific electronic configurations. It is the cooperative alignment of the dipoles associated with off-centering that leads to the proper ferroelectric properties of these ceramic materials (Fig. 1a). However, the restrictive chemistries of conventional ferroelectrics hinder the incorporation of magnetic moments, the coupling of which to a long-range polar state would allow for fast and low energy non-volatile multiferroic data storage technologies. Furthermore, the toxicity of lead and the desirability of flexible, wearable devices, motivates the search for new mechanisms of generating ferroelectric and multiferroic materials based on organic and metal-organic technologies.

An alternative paradigm exists for designing ferroelectric materials that involves combinations of non-polar orderings coupling together to collectively break inversion symmetry — known as “hybrid” improper ferroelectricity (Fig. 1b). First discussed in the context of layered inorganic perovskites [1,2], this approach provides a promising route to circumvent the restrictive design criteria for conventional ferroelectrics. Recent trends have focused on metal-organic perovskites, where molecular constituents may be used to enhance the chances of obtaining polar structures and achieve couplings to orbital and magnetic orderings [3]. Perovskite ferroelectrics that are entirely metal-free have now been reported [4] with ordering temperatures and magnitudes of spontaneous polarisation comparable to those of BaTiO₃. Even when the molecular constituents of the metal-organic perovskite themselves lack a dipole moment, their inclusion in crystal structures can still form an important part of the design strategy for novel improper ferroelectric materials [5].

Now, writing in *Nature Materials*, Miao and colleagues [6] report the design and synthesis of a ferroelectric material that operates at the intersection of these two paradigms. Mimicking the conventional approach of local inversion-symmetry breaking, they exploit in their design the ringlike molecule 15-crown-5, whose geometry cannot support an inversion centre (Fig. 1c). On settling into a single conformation at low temperature, these cyclic ethers collectively break the glide-plane symmetry of the high-temperature centrosymmetric structure, giving rise to a bulk polarisation. But this broken symmetry also allows for a secondary effect involving a sliding of the rings that induces a further improper ferroelectric contribution to the polarisation (Fig. 1d). Both contributions are additive along a direction normal to the ring planes, one reinforcing the other. This microscopic mechanism is supported by a combination of variable-temperature crystallographic measurements and density functional theory calculations.

The generation of polarisation oriented normal to the layering axis of the [Cd(15-crown-5)][Cd₂Cl₆] structure is better suited to device applications than the in-plane polarisation generated by typical hybrid improper ferroelectrics. This is because most ferroelectric device architectures operate with fields applied perpendicular to the flat surfaces of a layered sample. Here it is also the case that the out-of-plane polarisation has allowed direct measurement of ferroelectric hysteresis in a bulk sample — something that has been difficult to achieve for many hybrid improper ferroelectrics and layered systems. Moreover, by applying a field bias using a piezo force microscope, Miao and colleagues show that it is possible to flip the polarisation of small domains, demonstrating direct external control over the sense of crown-ether ring orientations and direction of layer sliding in this responsive material.

Thinking beyond this specific system, further opportunities may exist to couple ring motions in metal-organic materials to novel kinds of ferroelectric order. Recent experimental evidence of unidirectional molecular spins in metal-organic frameworks [7] and computational predictions of cooperative rotations in porous framework materials [8] suggest a further route to ferroelectricity. While molecules such as 15-crown-5 possess a dipole moment described by a polar vector, a non-polar molecule spinning dynamically in a concerted manner breaks symmetry in a way that is described by an axial vector (Fig. 2a). Such axial vectors are used to describe magnetic moments (i.e. electron spins) and hence the same systematic symmetry-based design rules (Fig. 2b) used for predicting improper ferroelectric states based on

magnetic order [9] could help envisage further mechanisms by which polar distortions may be induced and enhanced using molecular spin.

Whether or not metal-organic ferroelectrics based on molecular spin order can be developed, the observation by Miao and colleagues [6] of switchable ferroelectric polarisation in van der Waals materials is a significant step towards functional device application. Particularly exciting is that the improper contribution to the polarisation is normal to the layering axis, which helps when applying an electric field to switch polarisation in device architectures. Further work will be required to enhance the magnitude of the ferroelectric response, and to replace cadmium with less toxic alternatives such as calcium or magnesium. However, the versatile chemistry of this class of materials, and the broad scope for a variety of symmetry-breaking mechanisms to be at play, make this a particular promising area of research.

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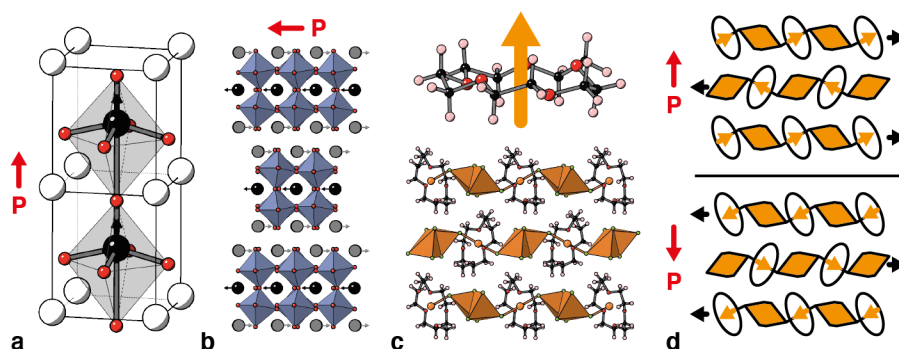


Figure 1 | Mechanisms for generating ferroelectricity. **a**, Proper ferroelectricity in PbTiO_3 arising from off-centre displacements of Ti^{4+} cations within the TiO_6 octahedra. Alignment of dipole vectors (black arrows) from neighbouring unit cells gives a net polarisation. **b**, Improper ferroelectricity in $\text{Ca}_3\text{Mn}_2\text{O}_7$ driven by two non-polar distortions (octahedral tilts and compositional order) that couple to displacements parallel to the natural layering axis. Anti-aligned polar displacements in the different layers (black and grey arrows) do not fully cancel out, giving a net polarisation. **c**, In the crystal structure of $[\text{Cd}(15\text{-crown-5})][\text{Cd}_2\text{Cl}_6]$, the acentric crown ether rings carry a local polarisation (orange arrow). Carbon, oxygen, and hydrogen atoms are shown as black, red, and pink spheres, respectively. These rings enclose Cd centres (orange circles) that connect chlorocadmiate columns (orange polyhedra). **d**, Schematic representation of the reversal of crown ether polarisation order and layer sliding upon polarisation inversion. In all instances, the bold red arrows indicate the direction of the spontaneous long-range net polarisation.

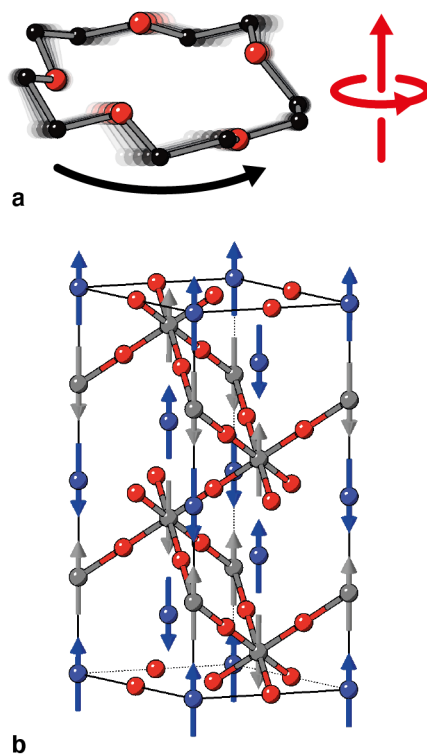


Figure 2 | Breaking inversion symmetry with axial vectors. **a**, A rotating molecule breaks symmetry in a manner captured by an axial vector parallel to the rotation axis (red arrows). **b**, Specific patterns of axial vector order can break inversion symmetry, such as in the example of collinear antiferromagnetic order shown here. Blue and grey arrows conventionally represent electron spin, but might equally well describe the sense of molecular spin.