Highlights

RESEARCH AREA 2 - Functional and Complex Materials for Innovative Electronics and Sensing - 2023

Near-90° Switch in the Polar Axis of Dion–Jacobson Perovskites by Halide Substitution

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Ferroelectricity in two-dimensional hybrid (2D) organic−inorganic perovskites (HOIPs) can be engineered by tuning the chemical composition of the organic or inorganic components to lower the structural symmetry and order−disorder phase change. Less efforts are made toward understanding how the direction of the polar axis is affected by the chemical structure, which directly impacts the anisotropic charge order and nonlinear optical response. To date, the reported ferroelectric 2D Dion−Jacobson (DJ) $[PbI_4]^{2-}$ perovskites exhibit exclusively out-of-plane polarization. Here, we discover that the polar axis in ferroelectric 2D Dion−Jacobson (DJ) perovskites can be tuned from the out-of-plane (OOP) to the in-plane (IP) direction by substituting the iodide with bromide in the lead halide layer. The spatial symmetry of the nonlinear optical response in bromide and iodide DJ perovskites was probed by polarized second harmonic generation (SHG). Density functional theory calculations revealed that the switching of the polar axis, synonymous with the change in the orientation of the sum of the dipole moments (DMs) of organic cations, is caused by the conformation change of organic cations induced by halide substitution.

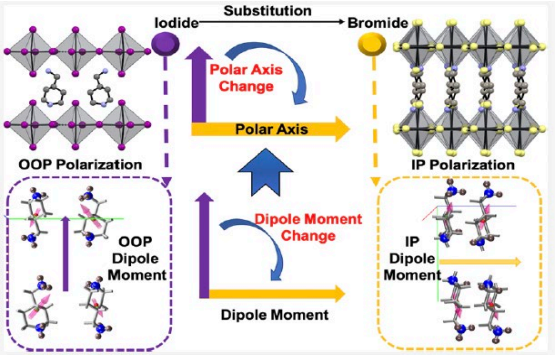

Fig.1 The polar axis in ferroelectric 2D Dion−Jacobson (DJ) perovskites can be tuned from the out-of-plane (OOP) to the in-plane (IP) direction by substituting the iodide with bromide in the lead halide layer.

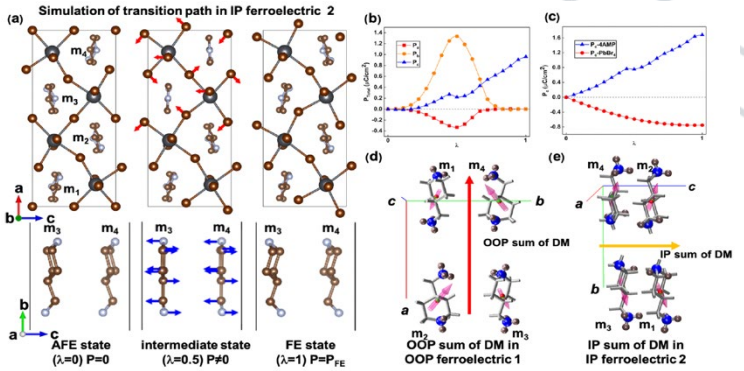

Fig.2 (a) Transition path in IP ferroelectric 2 from AFE (P = 0, λ = 0) to FE (+P, λ = 1) phases, containing the top view (along the b axis) of the perovskite inorganic lattice and side view (along the a axis) of 4AMP cations. m1−m4 indicate the four 4AMP molecules in the unit cell. The red arrows represent the direction of significant atomic displacements. The blue arrows indicate the converted path of 4AMP cations. (b) Total FE polarization as a function of λ in IP ferroelectric 2. (c) Polarization contribution of the 4AMP cations and inorganic lattice in IP ferroelectric 2. (d,e) Scheme of the sum dipole moment (DM) in OOP ferroelectric 1 and IP ferroelectric 2, respectively. Direction and size of the arrows illustrate the dipole orientation and magnitude, respectively.

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