Supporting Information

H/F Substitution Induced Switchable Coordination Bonds in a Cyano-Bridged Hybrid Double Perovskite Ferroelastic

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Methods

Single-crystal X-ray diffraction. Single-crystal X-ray diffraction data were measured using a Rigaku Saturn 924 diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Data collection, cell refinement, and data reduction was performed using Rigaku CrystalClear 1.3.5. The structures were solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXTL software package. All non-hydrogen atoms were refined anisotropically and the positions of all hydrogen atoms were generated geometrically. The data collection and structure refinement of these crystals are summarized in Table S1. The X-ray crystallographic structures have been deposited at the Cambridge Crystallographic Data Centre (deposition numbers CCDC 2131140-2131141) and can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/getstructures.

Powder X-ray diffraction. Powder X-ray diffraction (PXRD) data were measured using a Rigaku D/MAX 2000 PC X-ray diffraction system with Cu Kα radiation in the 2θ range of 5°–40° with a step size of 0.02°.

DSC and dielectric measurements. Differential scanning calorimetry (DSC) measurements were recorded on a NETZSCH DSC 200F3 instrument by heating and cooling crystalline samples with a rate of 10 K min^{-1} in aluminum crucibles at nitrogen atmosphere. Complex dielectric permittivities were measured with a TH2828A impedance analyzer. The samples were made with a pressed-powder pellet for dielectric measurements. Silver conductive paste deposited on the plate surfaces of samples was used as top and bottom electrodes.

Materials.

Synthesis of TMFM-Cl. Trimethylfluoromethyl ammonium chloride (TMFM-Cl) was synthesized by the reaction of equimolar amounts of trimethylamine (200 mmol, 30 wt % in water) and chlorofluoromethane (200 mmol) in ethanol (200 ml) at room temperature for 72h with stirring. Colorless solid samples of TMFM-Cl (70% yield) were obtained after the removal of the solvents under reduced pressure. Dried sample of TMFM-Cl was stored in a vacuum desiccator.

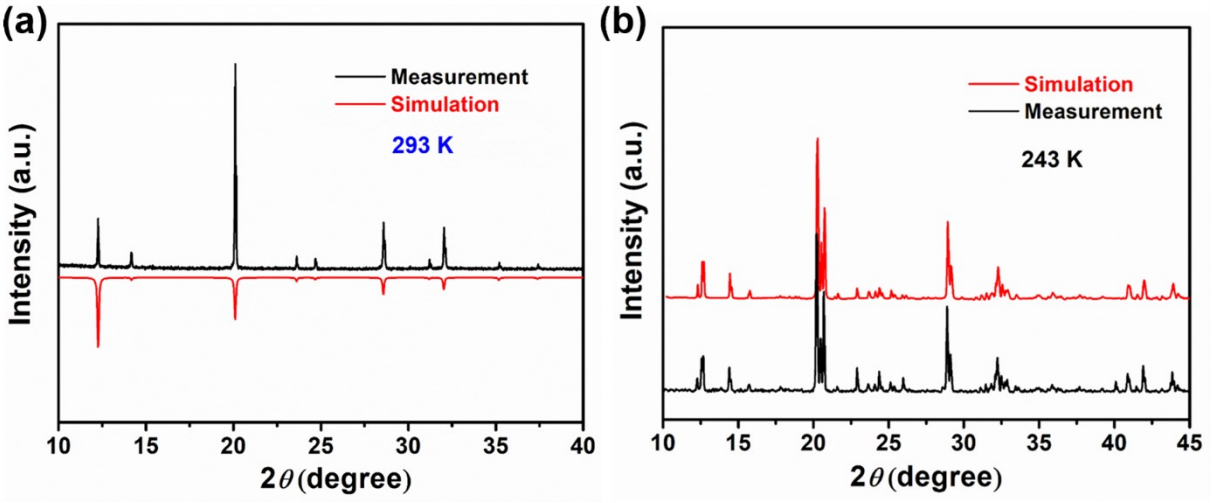

Fig. S1 PXRD patterns of TMFM-1 in (a) HTP and (b) LTP match well with those simulated from the single-crystal structures.

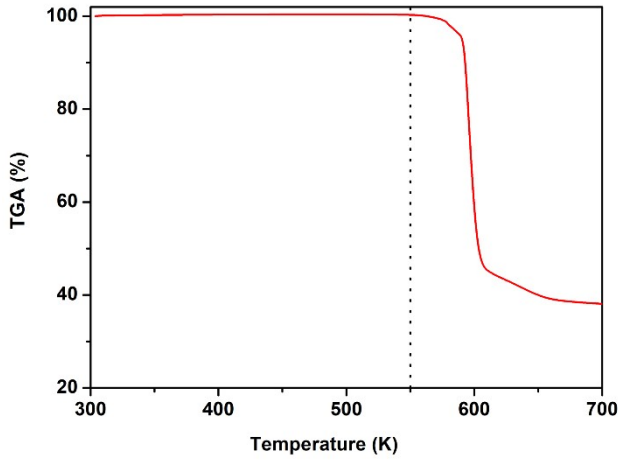

Fig. S2 TGA curve of TMFM-1.

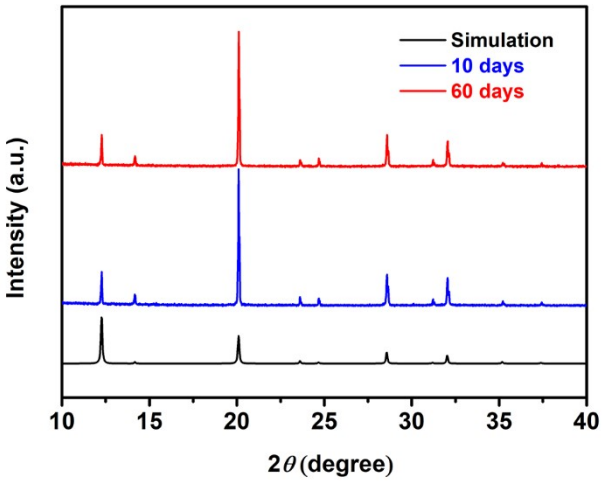

Fig. S3 PXRD patterns of TMFM-1 recorded after 10/60 days upon exposure to air at room temperature.

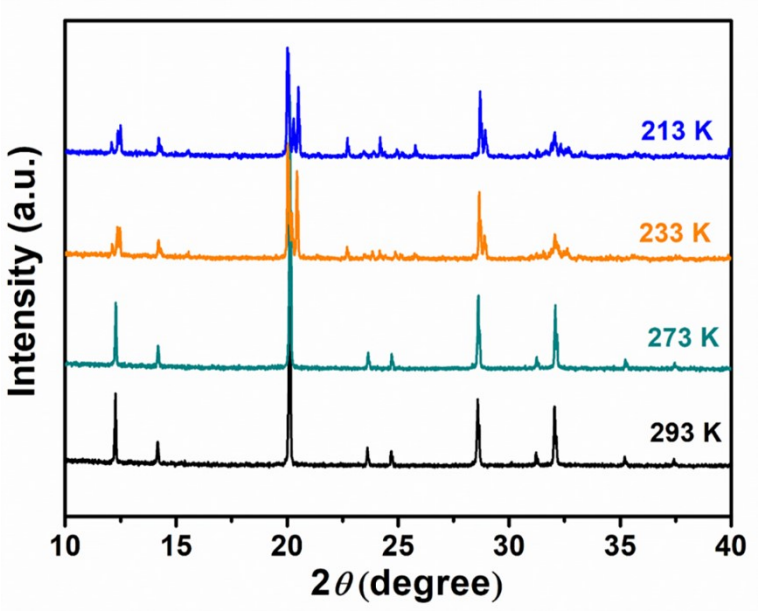

Fig. S4 Variable temperature PXRD patterns of TMFM-1.

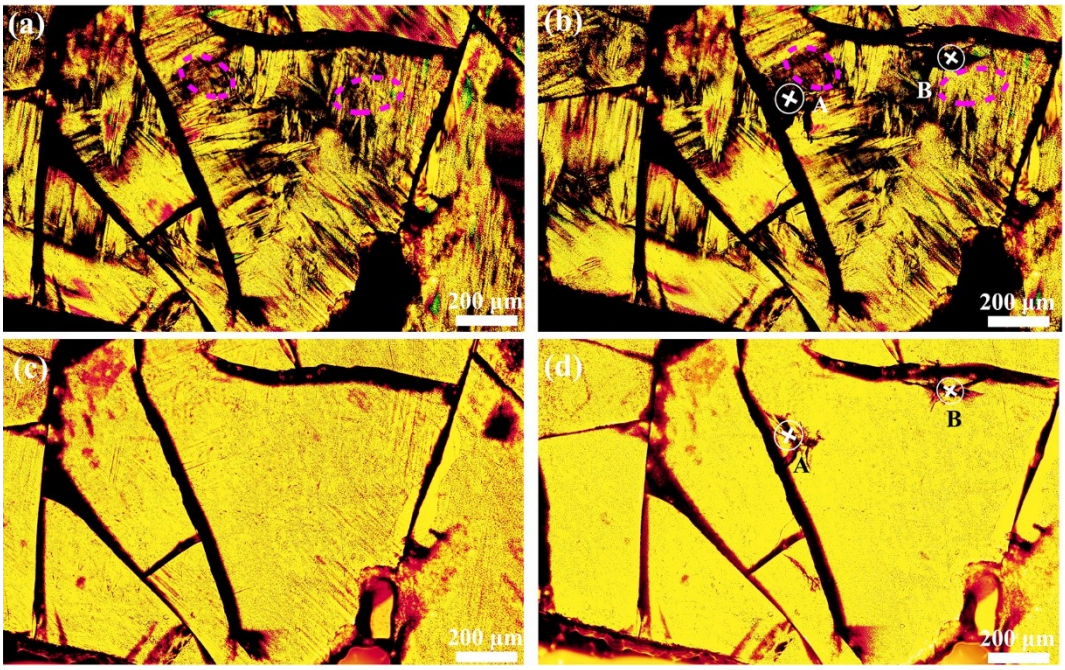

Fig. S5 (a, b) The observation of ferroelastic domains variation at 243 K before (a) and after (b) applying external strain. (c, d) Crystal surface morphology variation before (c) and after (d) applying external strain. The circle "×" indicates the position where the force is applied, the scale bar is 200 μm. There is a clear ferroelastic domains change at the red circle A and B, after applying external strain.

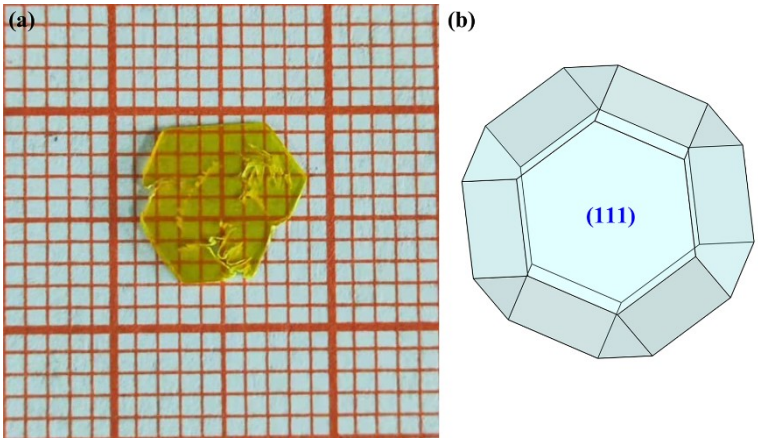

Fig. S6 The single crystal with a crystallographic orientation perpendicular to the (111) plane (a) and the simulated morphology of $[(CH_3)_3NCH_2F]_2[KFe(CN)_6]$ at 300 K.

Table S1. Crystal data and structural refinements for TMFM-1 at 243 K and 300 K.

Temperature	243 K	300 K
Formula	$[(CH_3)_3NCH_2F]_2[KFe(CN)_6]$	$[(CH_3)_3NCH_2F]_2[KFe(CN)_6]$
Weight	435.35	435.35
System	Monoclinic	Cubic
Space group	*C*2/*c*	*Fm*-3*m*
a (Å)	15.210(3)	12.4857(3)
b (Å)	8.7181(11)	12.4857(3)
c (Å)	15.206(3)	12.4857(3)
α (°)	90.00	90.00
β (°)	109.26(2)	90.00
γ (°)	90.00	90.00
V (Å^3)	1903.5(6)	1946.43(14)
Z	4	4
R_1	0.1657	0.0424
wR_2	0.3018	0.1369
GOF	1.057	1.046

Table S2 in revision. Summary of cyano-bridged dimetallic complexes with ferroelasticity.

Compound	Symmetry change	Ferroelastic domain	Reference
$[CH_3NH_3]_2[KFe(CN)_6]$	*m*-3*m*F2/*m*	not observed	[1]
$[(CH_3)_2NH_2]_2[KFe(CN)_6]$	*m*-3*m*F4/*mmm*	not observed	[1]
$[(CH_3)_3NH]_2[KFe(CN)_6]$	*m*-3*m*F2/*m*	not observed	[1]
$[(CH_3)_4N]_2[KFe(CN)_6]$	*m*-3*m* to 4/*m*	non-ferroelastic	[1]
$[formamidinium]_2[KFe(CN)_6]$	*m*-3*m*F-1	not observed	[2]
$[formamidinium]_2[KCo(CN)_6]$	*m*-3*m*F-1	not observed	[2]
$[(CH_3)_3NOH]_2[KFe(CN)_6]$	*m*-3*m* to *m*	not observed	[3, 4]
$[C(NH_2)_3]_2[KFe(CN)_6]$	*m*-3*m*F-3*m*	not observed	[5]
$[CH_3C(NH_2)_2]_2[KFe(CN)_6]$	*m*-3*m*F-3*m*, *m*-3*m*F2/*m*	observed	[5, 6]
$[CH_3C(NH_2)_2]_2[KCo(CN)_6]$	*m*-3*m*F-3*m*, *m*-3*m*F2/*m*	observed	[6]
$[CH_3C(NH_2)_2]_2[KCr(CN)_6]$	*m*-3*m*F-3*m*, *m*-3*m*F2/*m*	observed	[6]
$(imidazolium)_2[KFe(CN)_6]$	-3*m*F2/*m*	not observed	[7]
$(imidazolium)_2[KCo(CN)_6]$	-3*m*F2/*m*	not observed	[8]
$(imidazolium)_2[KFe_{0.42}Co_{0.58}(CN)_6]$	-3*m*F2/*m*	observed	[9]
$[(CH_3)_3NH]_2[KCo(CN)_6]$	*m*-3*m*F2/*m*	not observed	[10]
$[(CH_3)_2NH_2]_2[KCo(CN)_6]$	4/*mmm* to 4/*mmm*	non-ferroelastic	[11]
$[(CH_3)_2ND_2]_2[KCo(CN)_6]$	4/*mmm* to 4/*mmm*	non-ferroelastic	[11]
$[CH_3NH_3]_2[KCo(CN)_6]$	*m*-3*m*F2/*m*	not observed	[12]
$[CH_3NH_3]_2[NaCo(CN)_6]$	*m*-3*m*F2/*m*	not observed	[13]
$[C_3H_6NH_2]_2[KCo(CN)_6]$	*m*-3*m* to *m*-3*m*	non-ferroelastic	[14]
$[CH_3NH_3]_2[KCr(CN)_6]$	*m*-3*m*F2/*m*	observed	[15]
$[(CH_3)_2NH_2]_2[KCr(CN)_6]$	*m*-3*m*F4/*mmm*	observed	[16]
$(imidazolium)_2[RbCo(CN)_6]$	3*m* to 3 to 2/*m*	non-ferroelastic	[17]
$[(CH_3)_4N]_2[KHg(CN)_6]$	-43*m* to -4	non-ferroelastic	[18]
$[Pyrrolidinium]_2[KFe(CN)_6]$	-3*m*F2/*m*	not observed	[19]
$[Pyrrolidinium]_2[KCo(CN)_6]$	-3*m*F2/*m*	not observed	[19]
$[Pyrrolidinium]_2[KCr(CN)_6]$	*m*-3*m*F?	not observed	[20]
$[(CH_3)_3NOH]_2[KCo(CN)_6]$	*m*-3*m* to *m*	observed	[4, 21]
$[(CH_3)_3NCH_2F]_2[KFe(CN)_6]$	***m*-3*m*F2/*m***	**observed**	**this work**

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