Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

A three-dimensional Mn(II) coordination polymer with ferroelasticity by introducing coligands to form novel networks

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Measurements methods

Differential Scanning Calorimetry (DSC) Measurements and thermogravimetric analysis (TGA). The DSC measurement was performed by using a PerkinElmer Diamond DSC instrument. In a nitrogen atmosphere, the powder sample was studied in a temperature range of 300 to 420 K by heating and cooling. The sample of about 21 mg was placed in the aluminum crucibles. The heating and cooling rate are 20 K/min. Thermogravimetric analysis (TGA) were performed on a Netzsch Model TG209F1 instrument. The measurements were collected in nitrogen flow from 298 K to 1200 K at rate of 20 K/min.

Dielectric Measurements. Complex dielectric permittivity ε ($\varepsilon = \varepsilon' - i\varepsilon''$) was measured on a TonghuiTH2828A instrument at frequency, and the temperature range from 300 to 420 K. The electric field applied here was 1 V.

Single Crystal Structure Determination. Variable-temperature X-ray single-crystal diffraction data of **1** were collected on a Rigaku Saturn 924 diffractometer with Mo-Kα radiation (λ = 0.71073). All data processing, including empirical absorption corrections, was performed by using the Crystal-Clear software package. The crystal structures under HTP and LTP were solved by direct methods and refined by a full matrix method based on F^2 by means of the shelxtl-2014 package and Olex2 software. The molecular structure and stacking diagrams were drawn with the Diamond software.

Phase Purity. Infrared (IR) spectroscopy was employed on a Shimadzu model IR 60 spectrometer. Elemental analysis was performed on the Heraeus CHNO Rapid elemental analyzer. Powder X-ray diffraction (PXRD) analysis were performed on PANalyticalXPert PRO X-Ray Diffractometer at 293 K. The diffraction patterns were obtained within 2θ range of 5-50° with a step size of 0.02°.

Photoluminescence Measurements. The emission and excitation spectra in solid states were measured on an Edinburgh FLS-980 fluorescence spectrometer.

Ferroelastic measurement. For ferroelastic measurement, the domains were observed under an Olympus BX51TRF optical polarization microscope. The single-crystal sample with the thickness of 1 mm was placed on an INSTEC HCC602 cooling/heating stage. Before observing the ferroelastic domains, the crystal needs to be heated to about 400 K (HTP) and then cooled to room temperature for pretreatment.

First-Principles Calculations. The first-principles calculations in this paper are performed with the plane-wave pseudo-potential method based on density functional theory in CASTEP. The exchange and correlation are described by Perdew-Burke-Ernzerhof (PBE) in generalized-gradient approximation (GGA). The pseudopotential is selected as ultra-soft pseudopotential. And the default algorithm for geometry optimization is BFGS method. The Monkhorst-Pack methods are used for k point (6 × 6 × 3 for BCC or FCC, 8 × 8 × 2 for HCP) in Brillouin zone. The cutoff energy is chosen as 500 eV confirmed by convergence test. The structure is relaxed until residual forces per atom are smaller than 0.01 eV/Å, max placement of an atom is less than 0.0001 Å, max stress in crystal is no more than 0.05 GPa. Based on theoretical calculations, Voigt and Ruess bulk and shear moduli (B_V, G_V, B_R and G_R) can be obtained, more accurate bulk modulus (B) and shear modulus (G) are obtained based

on Hill's average:

$$B_H = \frac{B_V + B_R}{2}, \quad G_H = \frac{G_V + G_R}{2}.$$

The Young's modulus (E) and Poisson's ratio (v) can be calculated based on the bulk modulus and shear modulus:

$$E = \frac{9B_H G_H}{3B_H + G_H},$$

$$v = \frac{3B_H - 2G_H}{2(3B_H + G_H)}.$$

The universal anisotropic index (A^U), percent anisotropy (A_B and A_G) can be calculated:

$$A^U = 5\frac{G_V}{G_R} + \frac{B_V}{B_R} - 6, \quad A_B = \frac{B_V - B_R}{B_V + B_R}, \quad A_G = \frac{G_V - G_R}{G_V + G_R}.$$

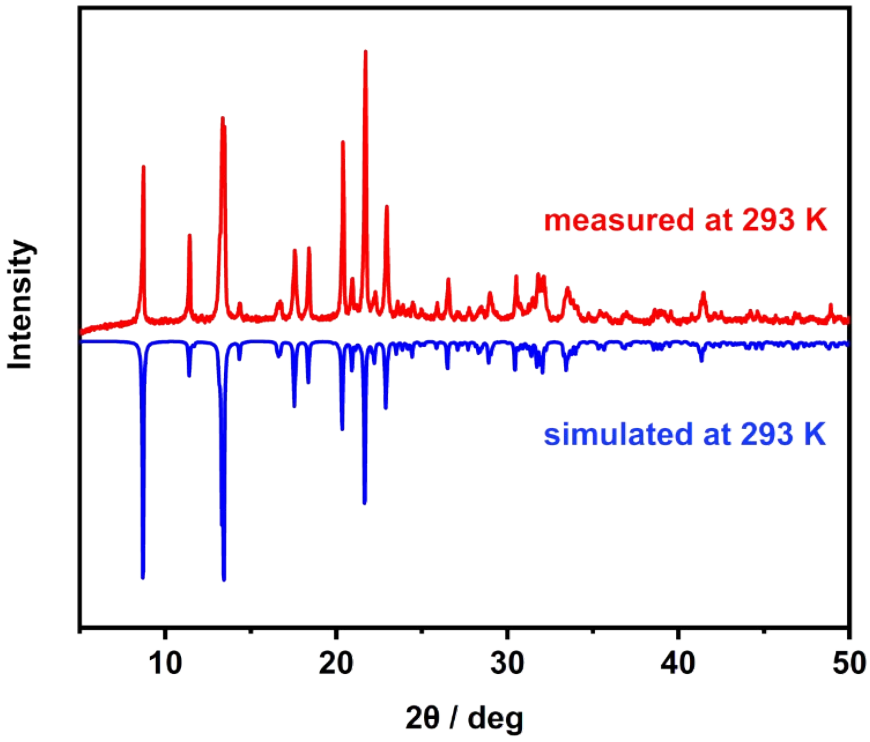

Figure S1. Powder X-ray diffraction patterns at 293 K.

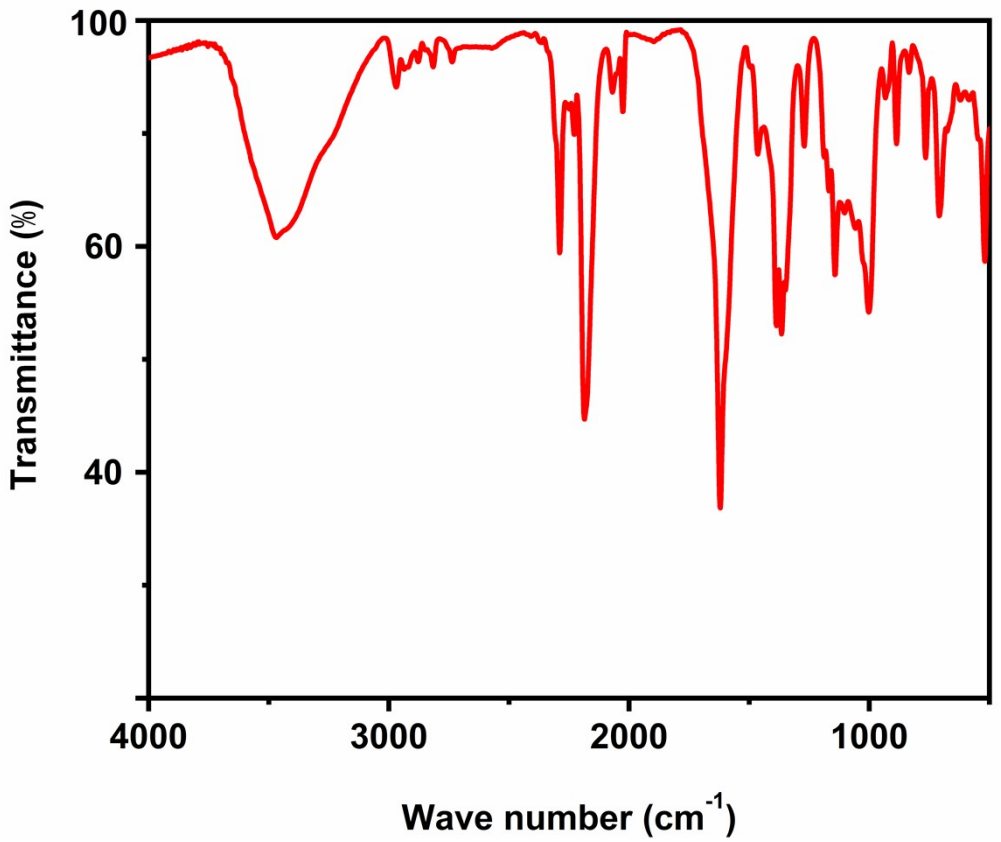

Figure S2. IR spectra of **1** measured at room temperature, where the strong signal at 3500 cm^{-1} is due to the moisture of the KBr used for IR.

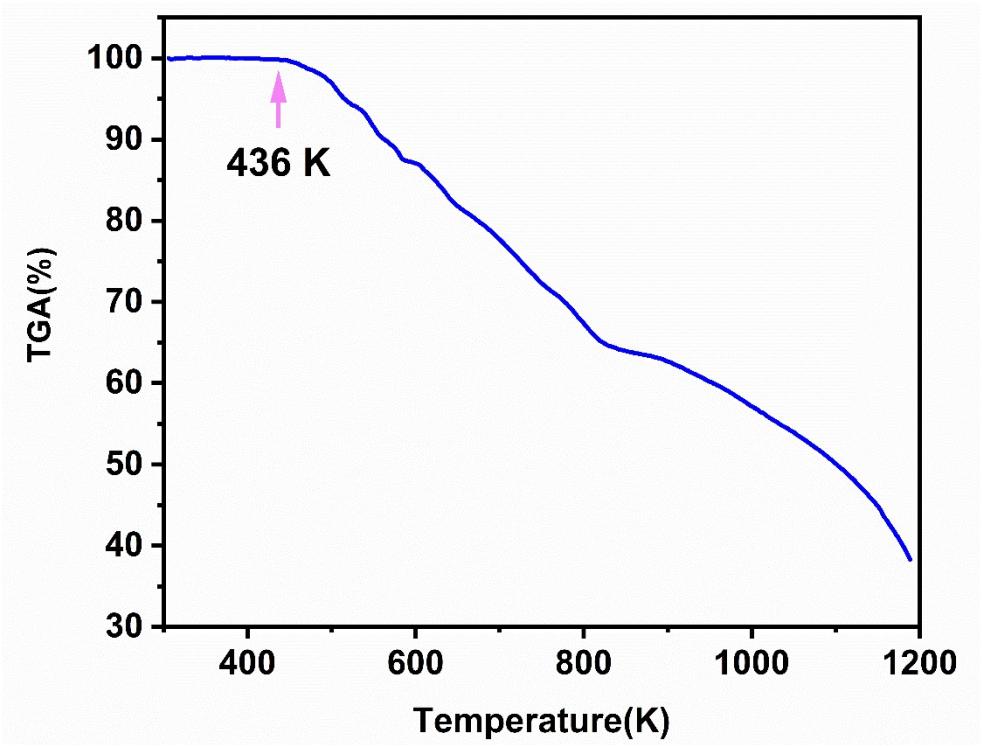

Figure S3. TGA curve of **1**.

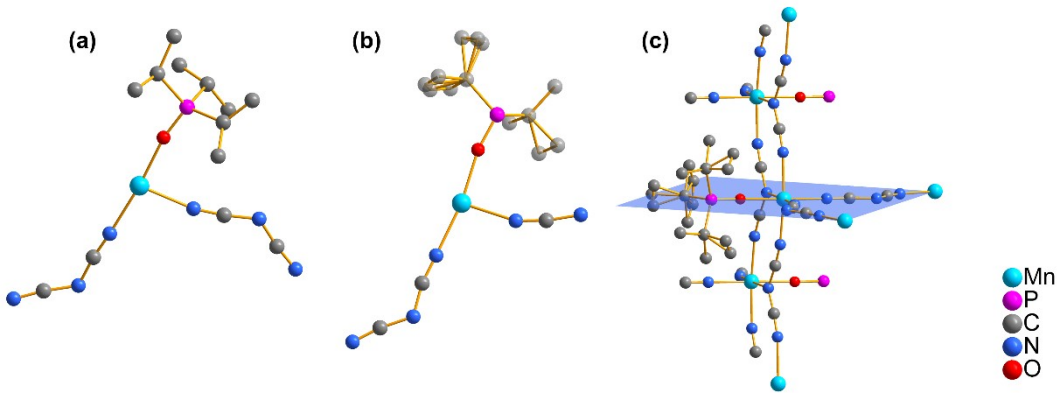

Figure S4. (a) Asymmetric unit of **1** in the LTP. (b) Asymmetric unit of **1** in the HTP. (C) Mirror plane and molecular structure diagram at HTP. The blue plane represents the mirror plane.

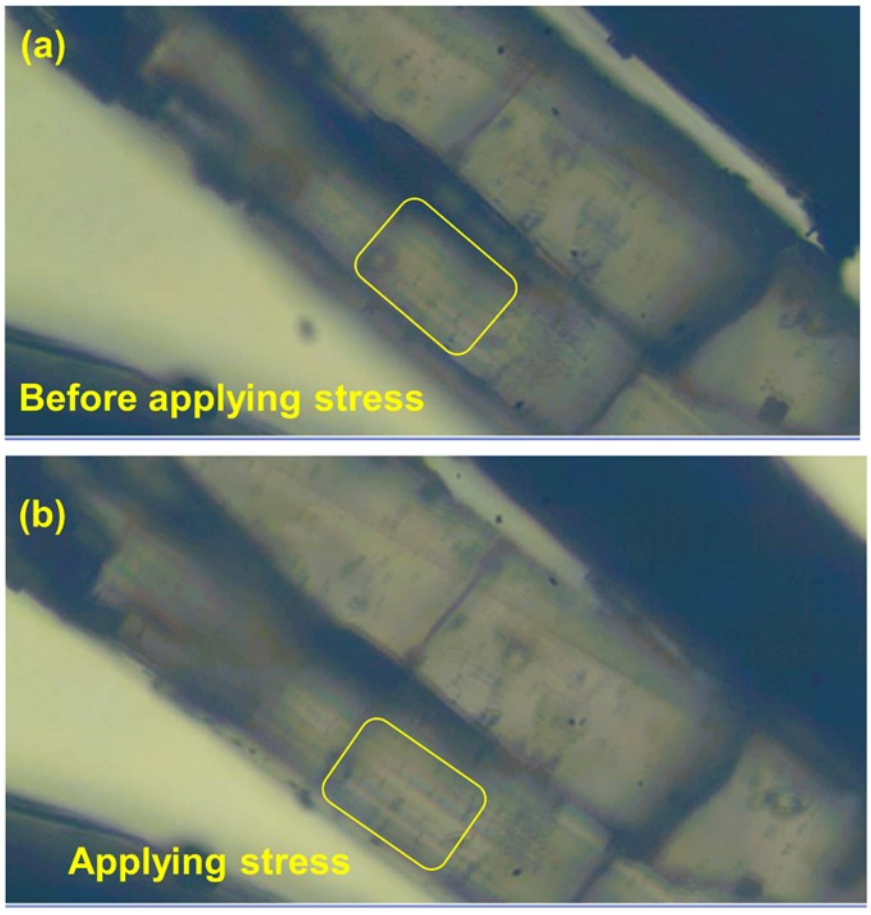

Figure S5. Enlarged view of the change in the ferroelastic domain before and after the application of stress.

Table S1. Crystal data and Refinement collected at different phases.

{Mn[(*i*-Pr)$_3$PO](dca)$_2$}		
T (K)	293 K	408 K
Formula weight	363.27	342.10
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	*Pmnb*
a/Å	8.7272 (6)	8.7333 (3)
b/Å	13.4618 (9)	13.8646 (7)
c/Å	15.5199 (9)	15.4301 (7)
α (deg)	90	90
β (deg)	90.731 (6)	90
γ (deg)	90	90
V/Å^3	1823.2 (2)	1868.33 (14)
Z	4	4
F (000)	756	748
GOF	1.11	1.04
R_1	0.073	0.071
wR_2	0.239	0.244

The computed results of the (3,5)-connected net of **1** by TOPOSPRO are as follows:

```
####################
1:C13 H21 Mn N6 O P
####################

Topology for ZB1
---------------------
Atom ZB1 links by bridge ligands and has
Common vertex with                                  R(A-A)
ZC 1      0.2542    -0.1202     1.0765    ( 1 0 2)    3.266A        1
ZC 1      0.7458     0.1202     0.9235    ( 0 0 0)    4.419A        1
ZC 1     -0.2542     0.1202     0.9235    (-1 0 0)    4.436A        1
Topology for ZC1
---------------------
Atom ZC1 links by bridge ligands and has
```

Common vertex with R(A-A)

ZB 1	0.7526	-0.0759	1.0472	(1 0 2)	3.266A	1
ZB 1	0.2474	0.0759	0.9528	(0 0 0)	4.419A	1
ZB 1	1.2474	0.0759	0.9528	(1 0 0)	4.436A	1
ZC 1	0.7542	0.6202	0.5765	(1 0 1)	8.621A	1
ZC 1	0.7542	-0.3798	0.5765	(1-1 1)	8.621A	1

Structural group analysis

Structural group No 1

Structure consists of 3D framework with ZCZB

Coordination sequences

ZB1: 1 2 3 4 5 6 7 8 9 10
Num 3 10 26 38 65 98 117 162 218 240
Cum 4 14 40 78 143 241 358 520 738 978

ZC1: 1 2 3 4 5 6 7 8 9 10
Num 5 12 24 44 65 90 129 164 200 260
Cum 6 18 42 86 151 241 370 534 734 994

TD10=986

Vertex symbols for selected sublattice

ZB1 Point symbol:{4^2.6}
Extended point symbol:[4.4.6(3)]

ZC1 Point symbol:{4^2.6^5.8^3}
Extended point symbol:[4.4.6.6.6.6.6.8(8).8(8).8(10)]

Point symbol for net: {4^2.6^5.8^3}{4^2.6}
3,5-c net with stoichiometry (3-c)(5-c); 2-nodal net

New topology, please, contact the authors (17896 types in 4 databases)
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