

Supporting Information

Ferroelastic Phase Transition with Large Spontaneous Strain Caused by Freezing the Conformational Dynamics of Ammonium

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Materials and Methods

All chemicals were reagent grade and used as being purchased without further purification. The XRPD spectra were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectrum was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the internet at <http://www.iucr.org>. Differential scanning calorimetry (DSC) measurements were performed on a NETZSCH Analyzing under nitrogen at atmospheric pressure with a heating/cooling rate of 5 K min⁻¹. Dielectric constant was measured with a Gwinstek LCR-meter over the frequency range of 500 Hz and 1 MHz at a heating/cooling rate of 2 K min⁻¹ from 100-300 to 270 K. The temperature of the sample was controlled by the liquid nitrogen thermostat with an East Changing TC280 Temperature Controller with uncertainty < 0.1 K. Variable-temperature polarization microscopy observations were carried out with a polarizing microscope NIKON LV100NPOL equipped with an INSTEC-HCS621XY cooling/heating stage THMSE 600. The temperature was stabilized with an accuracy of ±0.1 K.

SCXRD Data Collection and Structure Determinations.

The single-crystal X-ray diffraction data of **1-3** were collected on a Rigaku Xtlab-Min diffractometer at 293(2) K. The program CrysAlisPro 1.171.39.7e was used for the integration of the diffraction profiles. The structure was solved by direct method using the SHELXT program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL.¹ The non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F². All hydrogen atoms were generated theoretically at the specific atoms and refined isotropically with fixed thermal factors. The crystal data of **1-3** are summarized in Table S1. The selected bond lengths and angles are given in Table S2.

References

1 Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, C71, 3–8.

Table S1. Crystal data for **1**, **2** and **3**.

	1	2	3(RTP)	3(LTP)
Temperature/K	293 (2)	293(2)	293(2)	170(2)
Formulate	C ₁₉ H ₃₂ Fe ₆ N ₂ O ₃₆	C ₂₀ H ₃₄ Fe ₆ N ₂ O ₃₆	C ₂₃ H ₄₀ Fe ₆ N ₂ O ₃₆	C ₂₃ H ₄₀ Fe ₆ N ₂ O ₃₆
Weight	1199.56	1213.59	1255.67	1255.67
a/Å	28.903(4)	22.208(7)	23.1240(17)	6.8203(14)
b/Å	6.9208(11)	6.841(2)	6.9163(6)	11.744(3)

$c/\text{Å}$	20.641(5)	28.961(7)	28.584(2)	27.583(3)
$\alpha/^\circ$	90	90	90	82.650(14)
$\beta/^\circ$	105.589(17)	111.34(3)	107.658(7)	84.347(13)
$\gamma/^\circ$	90	90	90	76.202(18)
$V/\text{Å}^3$	3977.0(13)	4098(2)	4356.1(6)	2122.6(7)
space group	$I2/a$	$P2_1/c$	$C2/c$	P
Z	4	4	4	2
radiation type	MoK α	MoK α	MoK α	MoK α
$\rho(\text{g}/\text{cm}^3)$	2.003	1.967	1.915	1.965
Rint	0.1180	0.1358	0.0404	0.1754
Indep. ref. [I > 2 σ (I)]	9503	7057	3823	7383
Goodness of fit	1.091	0.993	1.100	0.969
R^1/wR^2 [I > 2 σ (I)]	0.1284/0.2718	0.0983/0.2049	0.0319/0.0718	0.1358/0.2954

$${}^a R_1 = \sum \|F_o\| - |F_c| / \sum \|F_o\| \quad {}^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2 \}^{1/2}$$

Table S2. Selected bond lengths [Å] and angles [°] for **1** and **2** and **3**.

	1		2		3(RTP)		3(LTP)	
Fe1-O004	1.939(11)	Fe4-O19	1.954(6)	Fe00-O1	1.938(2)	Fe5-O25	2.006(11)	
Fe1-O13	1.993(12)	Fe4-O32	2.019(6)	Fe00-O6	2.025(3)	Fe5-O31	2.012(12)	
Fe1-O11	2.022(12)	Fe4-O21	2.018(8)	Fe00-O4	2.032(3)	Fe5-O19	1.946(12)	
Fe1-O9	2.005(13)	Fe4-O30	2.021(8)	Fe00-O15	2.022(3)	Fe5-O32	2.032(12)	
Fe1-O7	2.017(12)	Fe4-O29	2.019(8)	Fe00-O8	2.021(3)	Fe5-O27	2.043(12)	
Fe1-O6	2.036(13)	Fe4-O22	2.015(8)	Fe00-O16	2.019(3)	Fe5-O28	2.029(11)	
Fe3-O004	1.909(10)	Fe6-O19	1.935(6)	Fe1-O1	1.906(2)	Fe2-O11	2.032(12)	
Fe3-O8	2.037(13)	Fe6-O25	2.047(7)	Fe1-O13	2.022(3)	Fe2-O5	2.021(12)	
Fe3-O1	2.009(12)	Fe6-O27	1.997(8)	Fe1-O17	2.008(3)	Fe2-O12	2.028(12)	
Fe3-O17	2.084(13)	Fe6-O34	2.013(8)	Fe1-O10	2.026(3)	Fe2-O14	2.016(12)	
Fe3-O5	2.012(13)	Fe6-O31	2.031(7)	Fe1-O18	2.083(3)	Fe2-O1	1.933(12)	
Fe2-O004	1.927(11)	Fe6-O28	2.030(8)	Fe1-O14	2.016(3)	Fe2-O2	2.032(12)	
Fe2-O4	2.025(13)	Fe2-O1	1.903(7)	Fe03-O1	1.929(2)	Fe1-O13	2.037(12)	
Fe2-O10	2.033(13)	Fe2-O18	2.072(7)	Fe03-O11	2.048(3)	Fe1-O10	2.012(13)	
Fe2-O12	2.020(13)	Fe2-O2	2.011(8)	Fe03-O7	2.027(3)	Fe1-O9	2.051(12)	
Fe2-O2	2.041(13)	Fe2-O6	2.016(8)	Fe03-O12	2.024(3)	Fe1-O1	1.943(11)	
Fe2-O15	2.028(14)	Fe2-O5	1.998(9)	Fe03-O9	2.013(3)	Fe1-O7	2.010(13)	
Fe3-O004-Fe1	119.7(6)	Fe2-O8	2.013(8)	Fe03-O2	2.006(3)	Fe1-O18	2.089(11)	
Fe3-O004-Fe2	119.5(6)	Fe1-O1	1.933(7)	Fe1-O1-Fe00	119.97(12)	Fe4-O19	1.902(12)	
Fe2-O004-Fe1	120.8(5)	Fe1-O3	2.042(7)	Fe1-O1-Fe03	119.94(12)	Fe4-O24	2.011(11)	

Fe1-O4	2.009(8)	Fe03-O1-Fe00	120.09(13)	Fe4-O21	2.020(13)
Fe1-O14	1.994(8)			Fe4-O36	2.090(12)
Fe1-O11	2.023(8)			Fe4-O26	2.055(12)
Fe1-O12	2.016(9)			Fe4-O22	2.036(12)
Fe3-O16	2.034(7)			Fe3-O6	2.055(13)
Fe3-O9	2.005(8)			Fe3-O3	1.995(13)
Fe3-O7	2.004(8)			Fe3-O8	2.054(12)
Fe3-O1	1.941(6)			Fe3-O1	1.903(12)
Fe3-O13	1.984(9)			Fe3-O16	2.031(13)
Fe3-O10	2.019(9)			Fe3-O4	2.005(12)
Fe5-O19	1.886(6)			Fe6-O19	1.945(12)
Fe5-O36	2.106(7)			Fe6-O30	2.022(12)
Fe5-O26	2.003(8)			Fe6-O23	2.042(12)
Fe5-O24	2.040(8)			Fe6-O29	2.042(12)
Fe5-O20	1.995(8)			Fe6-O34	1.991(13)
Fe5-O23	2.027(8)			Fe6-O20	2.034(13)
Fe6-O19-Fe4	118.8(3)			Fe5-O19-Fe6	119.5(6)
Fe5-O19-Fe4	120.9(3)			Fe4-O19-Fe5	121.0(6)
Fe5-O19-Fe6	120.2(3)			Fe4-O19-Fe6	119.4(6)
Fe1-O1-Fe3	119.4(3)			Fe2-O1-Fe1	119.2(6)
Fe2-O1-Fe3	120.5(4)			Fe3-O1-Fe2	121.5(6)
Fe2-O1-Fe1	120.1(3)			Fe3-O1-Fe1	119.3(6)

Table S3 Hydrogen bond data for complex 1.

D-H-A	d(D-H)(Å)	d(H..A)(Å)	<DHA(°)	d(D..A)(°)
O17-H17A...O14 ⁱ	0.866	1.979	166.71	2.829
O17-H17B...O16 ^{iv}	0.869	1.954	151.72	2.750
N1-H1A...O14 ⁱⁱ	0.890	2.092	138.76	2.822
N1-H1B...O8 ⁱⁱⁱ	0.890	2.207	156.52	3.044
N1-H1C...O15	0.890	1.992	173.82	2.878

Symmetry code: ⁱ-x+1, -y+1, -z; ⁱⁱ-x+1, y+1/2, -z+1/2; ⁱⁱⁱx, -y+1/2, z+1/2; ^{iv}-x+3/2, -y+1/2, -z+1/2.

Table S4 Hydrogen bond data for complex 2.

D-H-A	d(D-H)(Å)	d(H..A)(Å)	<DHA(°)	d(D..A)(°)
O36-H36A...O17	0.865	1.988	141.68	2.720
O36-H36B...O35 ^v	0.865	1.849	172.24	2.709

O18-H18A...O33	0.85	1.887	160.36	2.702
O18-H18B...O33	0.851	1.891	160.21	2.701
N1-H1A...O14 ⁱⁱ	0.890	2.163	136.16	2.872
N1-H1B...O23 ^{vi}	0.890	2.487	116.12	2.988
N1-H1C...O17 ⁱ	0.890	2.039	153.18	2.862
N2-H2A...O34 ⁱⁱⁱ	0.890	1.989	160.31	2.843
N2-H2B...O33	0.890	1.915	149.16	2.718

Symmetry code: ⁱ x, 1/2-y, 1/2+z; ⁱⁱ -x, -y, 1-z; ⁱⁱⁱ 1-x, 1-y, 1-z; ^{iv} 1-x, -1/2+y, 1/2-z; ^{vi} x, 3/2-y, 1/2+z

Table S5 Hydrogen bond data for complex **3 (RTP)**.

D-H-A	d(D-H)(Å)	d(H..A)(Å)	<DHA(°)	d(D..A)(°)
O18-H18A...O3 ^v	0.878	1.822	166.44	2.684
O18-H18B...O5 ^{iv}	0.880	1.886	159.85	2.729
N2-H2C...O5 ⁱⁱⁱ	0.890	2.110	167.09	2.984
N2-H2D...O14 ^{iv}	0.890	2.329	144.05	3.094
N1-H1E...O3 ⁱ	0.890	2.191	158.41	3.037
N1-H1D...O5 ⁱⁱ	0.890	1.803	155.42	2.639

Symmetry code: ⁱ x+1/2, -y+5/2, z+1/2; ⁱⁱ 1-x, 1+y, 3/2-z; ⁱⁱⁱ x, 1+y, z; ^{iv} -x+1, -y+2, -z+1; ^v 1/2-x, 1/2+y, 1/2-z.

Table S6 Hydrogen bond data for complex **3 (LTP)**.

D-H-A	d(D-H)(Å)	d(H..A)(Å)	<DHA(°)	d(D..A)(°)
O36-H36A...O17	0.910	1.782	172.55	2.687
O36-H36B...O33 ^{vi}	0.905	1.796	153.52	2.637
O18-H18A...O35 ^v	0.930	1.963	133.09	2.685
O18-H18B...O15 ^{iv}	0.930	1.879	145.39	2.697
N1-H1A...O35 ⁱⁱⁱ	0.890	2.169	151.53	2.982
N1-H1B...O26 ⁱⁱ	0.890	2.271	173.99	3.157
N2-H2A...O15	0.890	1.925	149.89	2.732
N2-H2B...O16 ⁱ	0.890	2.105	151.58	2.919

Symmetry code: ⁱ -x+1, -y+2, -z+1; ⁱⁱ -x, -y+2, -z+1; ⁱⁱⁱ -x, -y+1, -z+1; ^{iv} -x+2, -y+1, -z+1; ^v x+1, y, z; ^{vi} -x, -y+2, -z+2.

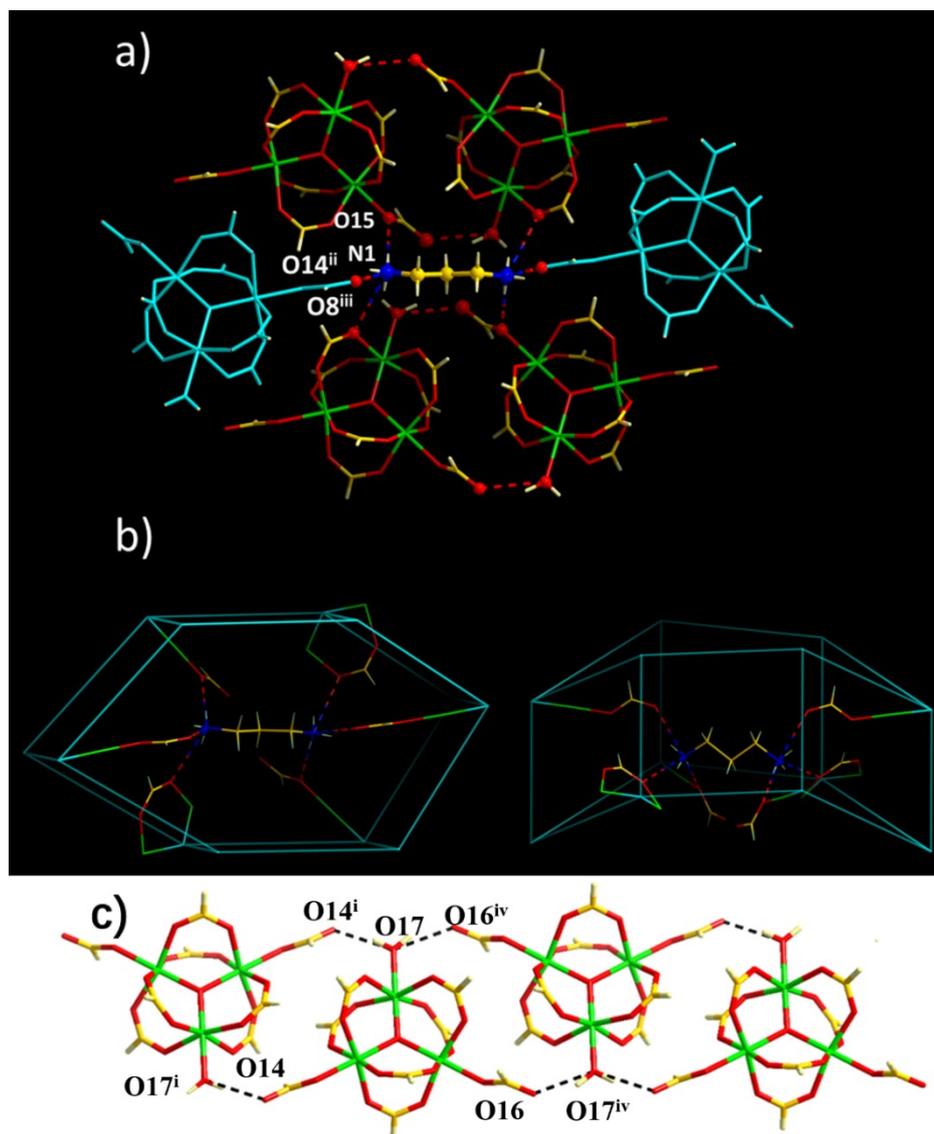


Fig.S1 (a) The H-bonds between the diammonium and $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ cluster in **1**. (b) Top (left) and side (right) view spindle like cavity formed by twelve $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ clusters with PDA filled in. (c) The 1D H-bonds formed by the $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ cluster in **1**. Symmetry code: ⁱ-x+1, -y+1, -z; ⁱⁱ-x+1, y+1/2, -z+1/2; ⁱⁱⁱx, -y+1/2, z+1/2; ^{iv}-x+3/2, -y+1/2, -z+1/2.

1 crystallized in $I2/a$ space group (Table S1) with one $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ and half PDA in the asymmetric unit. In the complex, a triangular $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_6]$ units are constructed by one $\mu_3\text{O}^{2-}$ anions and six *syn,syn* formates, then the unsaturated coordination sites of the triangular units are taken by two monodentate formate and one water in forming a negative charged cluster. The detail of the coordinated bond lengths was summarized in Table S2. The H-bonds between the water and the monodentate formate linked the anionic clusters to forming a 1D supramolecular chain (Fig. S1 and Table S3). In **1** the PDA have a staggered conformation belonging to $C2v$ point group with the center located at a 2-fold axis (Fig. S1a). Around the PDA there are twelve $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ clusters forming a confined spindle like cavity (Fig. S1b). In the cavity the PAD is stabilized orderly by H-bonds to six $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ clusters. The N1 atoms connected to three different oxygen atoms O8ⁱⁱⁱ, O14ⁱⁱ and O15, in which the O8ⁱⁱⁱ came from a *syn,syn* formate, O14ⁱⁱ is from the uncoordinated oxygen atoms of the monodentate formate and O15 is from coordinated oxygen atoms of the monodentate formate.

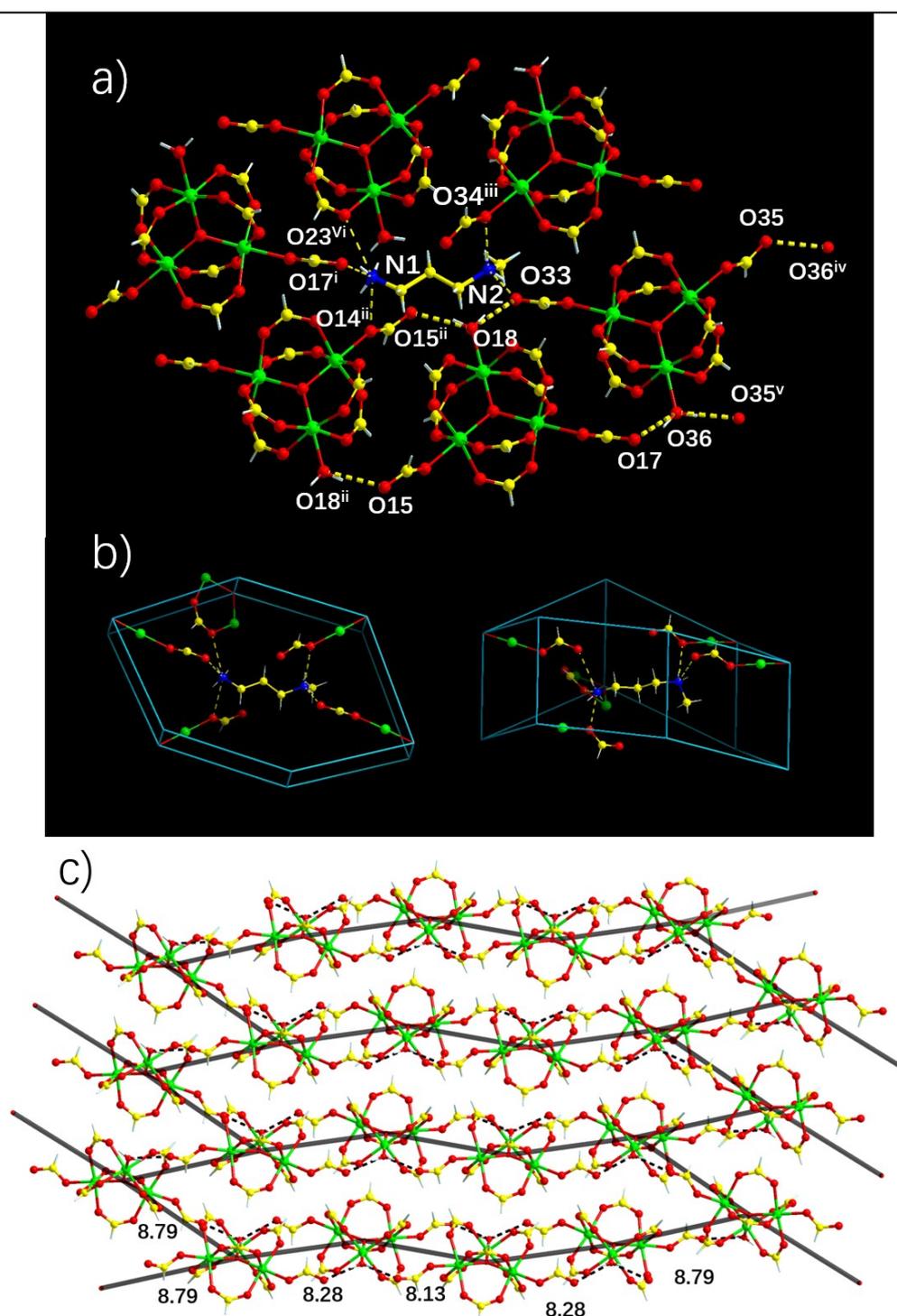


Fig. S2 (a) The H-bonds between the diammonium and [Fe₃O(O₂CH)₈(H₂O)] clusters in **2**. (b) Top (left) and side (right) view spindle like cavity formed by twelve [Fe₃O(O₂CH)₈(H₂O)] clusters with MPDA filled in. (c) The 6³ H-bond net formed by the [Fe₃O(O₂CH)₈(H₂O)] clusters in **2**. Symmetry code: ⁱ x, 1/2-y, 1/2+z; ⁱⁱ -x, -y, 1-z; ⁱⁱⁱ 1-x, 1-y, 1-z; ^{iv} 1-x, 1/2+y, 1/2-z; ^v 1-x, -1/2+y, 1/2-z; ^{vi} x, 3/2-y, 1/2+z.

2 crystallized in P2₁/c space group (Table S1) with two [Fe₃O(O₂CH)₈(H₂O)] clusters and one MPDA in the asymmetric unit. In the complex, the triangular [Fe₃O(O₂CH)₆] units are constructed by one μ₋₃ O²⁻ anions and six *syn,syn* formates, then the unsaturated coordination sites of the triangular units are taken by two monodentate formate and one water in forming a negative charged cluster like that in **1**. The detail of the coordinated bond lengths was summarized in Table S2. In **2**, the two type of [Fe₃O(O₂CH)₈(H₂O)] clusters connect to neighbor clusters through H-bonds in different ways. The first type cluster containing O18 connects to two neighbor clusters both through double H-bonds (O18...O33, O17...O36 and O18...O15ⁱⁱ, O15...O18ⁱⁱ) (Fig. S2a and Table S4). While the other cluster containing O36 links to three clusters through double (O36...O17 and O33...O18) and two single H-bonds (O36...O35^v and O35...O36^{iv}). Around the MPDA there are twelve [Fe₃O(O₂CH)₈(H₂O)] clusters forming a confined spindle like cavity (Fig. S2b). In the cavity the MPAD is stabilized orderly by H-bonds to five [Fe₃O(O₂CH)₈(H₂O)] clusters. The N1 atoms connected to three different oxygen atoms O14ⁱⁱ, O23^{vi} and O17ⁱ, in which the O23^{vi} came

from a *syn,syn* formate, O17ⁱ is from the uncoordinated oxygen atoms of the monodentate formate and O14ⁱⁱ is from coordinated oxygen atoms of the monodentate formate. The N2 atoms connected to two different oxygen atoms O34ⁱⁱⁱ, O33, in which the O33 came from the uncoordinated oxygen atoms of the monodentate formate and O34ⁱⁱⁱ is from coordinated oxygen atoms of the monodentate formate.

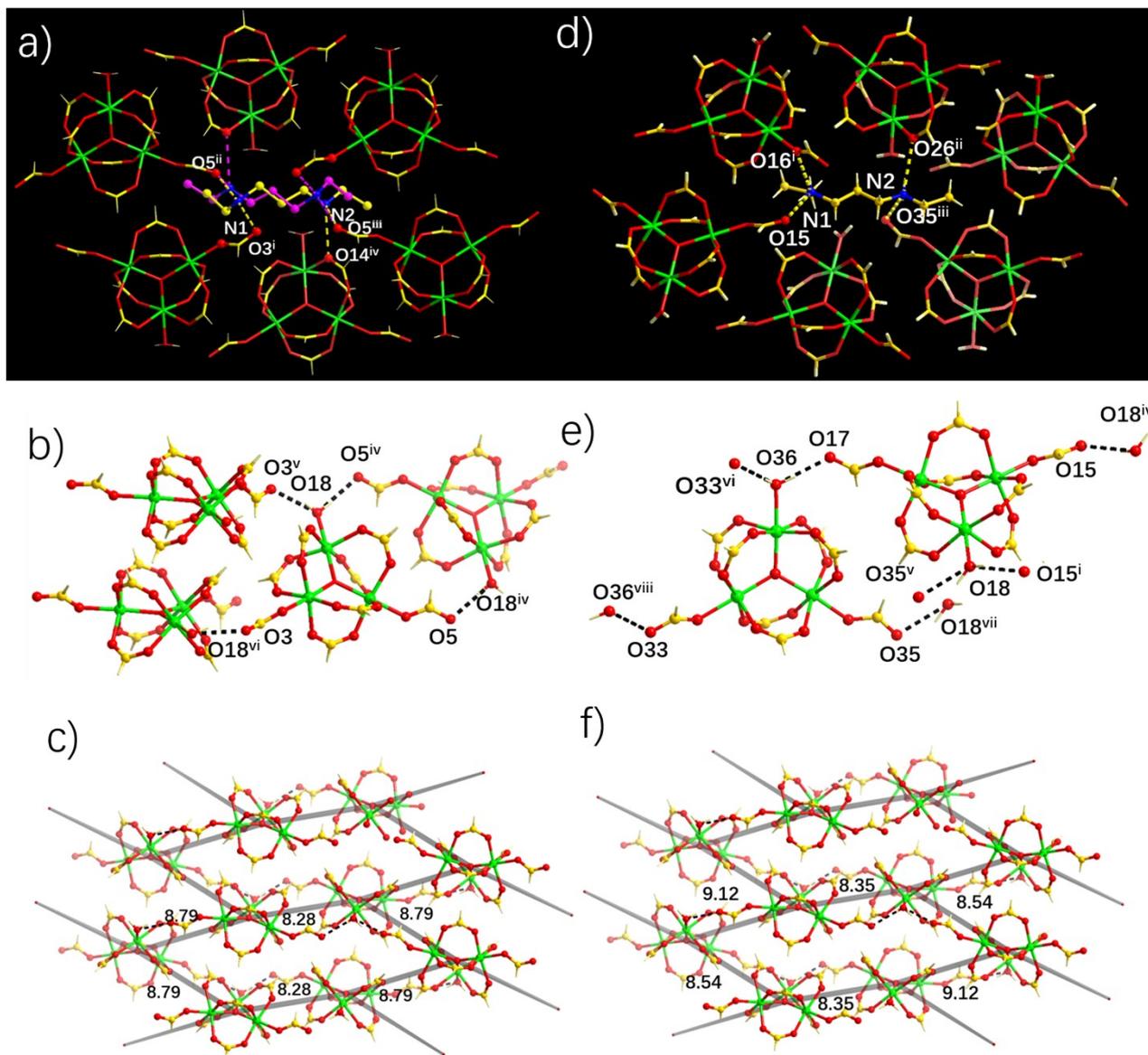


Fig.S3 (a) H-bonds linkage of the DEPDA and the $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ clusters in **3** at RTP. (b) H-bonds between the $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ clusters in **3** at RTP. (c) The 6^3 H-bond net formed by the $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ cluster in **3** at RTP. Symmetry code: ⁱ $x+1/2, -y+5/2, z+1/2$; ⁱⁱ $1-x, 1+y, 3/2-z$; ⁱⁱⁱ $x, 1+y, z$; ^{iv} $-x+1, -y+2, -z+1$; ^v $1/2-x, 1/2+y, 1/2-z$; ^{vi} $1/2-x, -1/2+y, 1/2-z$. (d) H-bonds linkage of the DEPDA and the $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ clusters in **3** at LTP. (e) H-bonds between the $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ clusters in **3** at LTP. (f) The 6^3 H-bond net formed by the $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ cluster in **3** at LTP. Symmetry code: ⁱ $-x+1, -y+2, -z+1$; ⁱⁱ $-x, -y+2, -z+1$; ⁱⁱⁱ $-x, -y+1, -z+1$; ^{iv} $-x+2, -y+1, -z+1$; ^v $x+1, y, z$; ^{vi} $-x, -y+2, -z+2$; ^{vii} $x-1, y, z$; ^{viii} $-x, 2-y, 2-z$.

At RTP the structure of **3** is very like that of **1** and **2** (Fig. S3a), and the asymmetric unit of **3** have one anionic $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ cluster and half DEPDA cation. However, the H-bonds in **3** at RTP is different like that of in **1**, the two $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ units connected to each other by the two H-bonds formed between the atom O5^{iv} of monodentate formate and water O18 as well as its symmetrically related atoms (Fig. S3b). Then the H-bond between the water O18 and O3^v of another monodentate formate linked units supramolecular Fe_6 connected to four others in forming a 6^3 H-bond layer with $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ as node (Fig. S3b and Fig. S3c). The DEPDA filled in the space of the H-bond layers. Different from that in **1**, at room temperature the DEPDA in **3** is disordered. The disordered DEPDA in **3** could be modeled as one molecule but have an orientational disorder to fulfill the requirements of the crystal symmetry (Fig. 1a). In **3** the linkage of the N2 atoms and the ethyl groups gives a gauche conformation. Thus, as one molecule alone the DEPDA belongs to C_1 point group and thus has only one symmetry element (E), in which the N1 and N2 linked the alkyl groups in forming gauche and staggered conformations respectively. And in the crystal the DEPDA have a pseudo C_2 symmetry, sharply differing from the C_{2v} symmetric of PDA. At RTP each EDPDA linked four $[\text{Fe}_3\text{O}(\text{O}_2\text{CH})_8(\text{H}_2\text{O})]$ clusters through the H-bond between the nitrogen atoms and the oxygen atoms of the ammonium and formates, in which

N1 connected to O3ⁱ and O5ⁱⁱ of the two monodentate formate and N2 connected to O14^{iv} and O5ⁱⁱⁱ of one monodentate formate and one *syn,syn* formate through H-bonds (Table S5). And from Fig. 1b, it is easily found, the DEPDA also filled in a spindle like cavity formed by twelve [Fe₃O(O₂CH)₈(H₂O)] clusters. However, the shape of the cavity in **3** is different with that in **1**. In **1** six [Fe₃O(O₂CH)₈(H₂O)] clusters are almost in one plan on the top or bottom, while in **3** the middle part of the shuttle-like cavity is upturned. And the N1 atoms connected to the two clusters located at the top of the cavity, while the N2 atoms connected to two triangle clusters on the bottom right corner and upper right corner. For the orientation disorder, in the cavity the DEPDA connected to six triangle clusters through the H-bonds (Fig. 3d and Table S6), in which four of the cluster located at the top of the cavity while two clusters located at the bottom of the cavity.

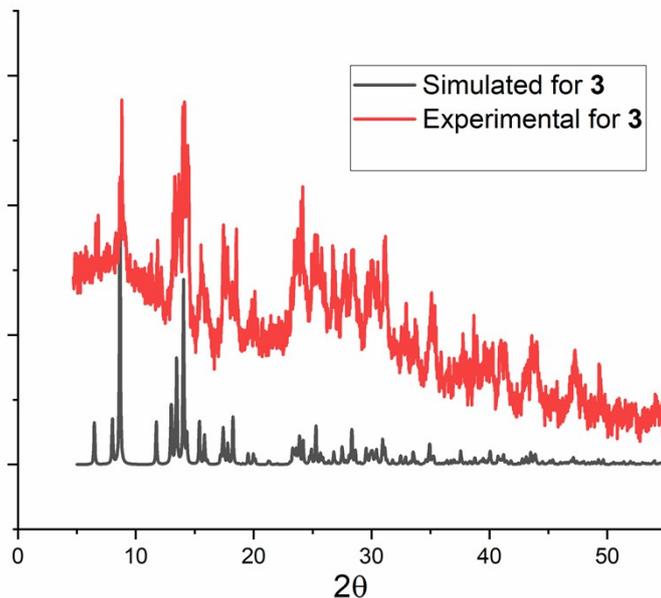


Fig.S4 Powder X-ray diffraction pattern of **3**.

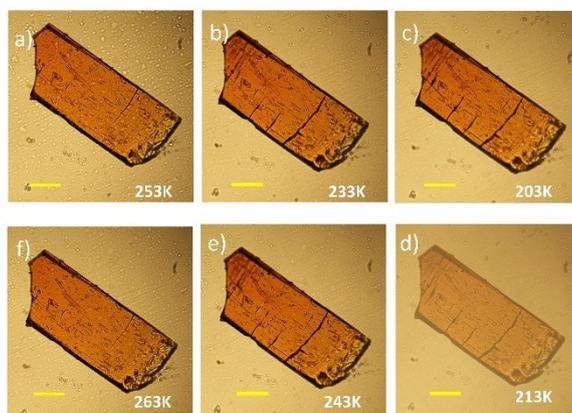


Fig. S5 Transmitted optical photograph of the crystal of **3** variation in the continuous cooling (a)-(c) and heating (d)-(f) process, the scale bar is 100 μm .