Supporting information for:

A prominent dielectric material with extremely high-temperature and reversible phase transition in the high thermally stable perovskite-like architecture

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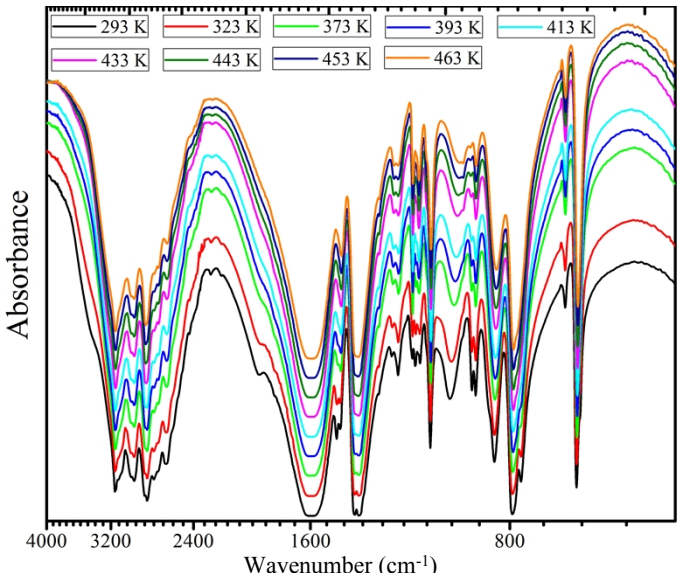

Fig. S1 IR spectra of compound 1 recorded at various temperatures corresponding to the spectral range 4000- 450 cm^{-1}.

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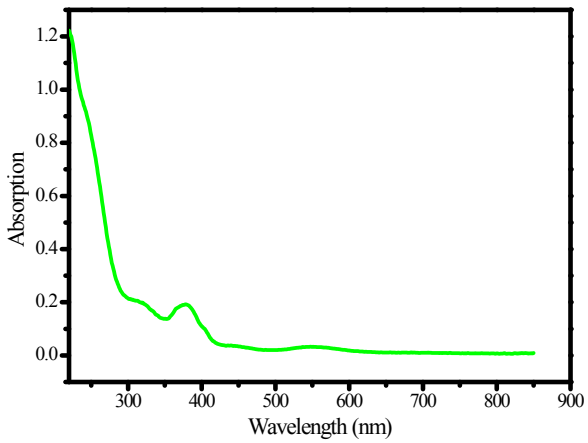

Fig. S2 Solid- state UV- Vis reflectance spectrum of compound 1.

The UV- Vis absorption spectrum for compound 1 was recorded in reflectance mode in the solid state at room temperature. According to the spectrum, the wavelength absorption edge of compound 1 occurs at approximately 378 nm (3.3 eV).

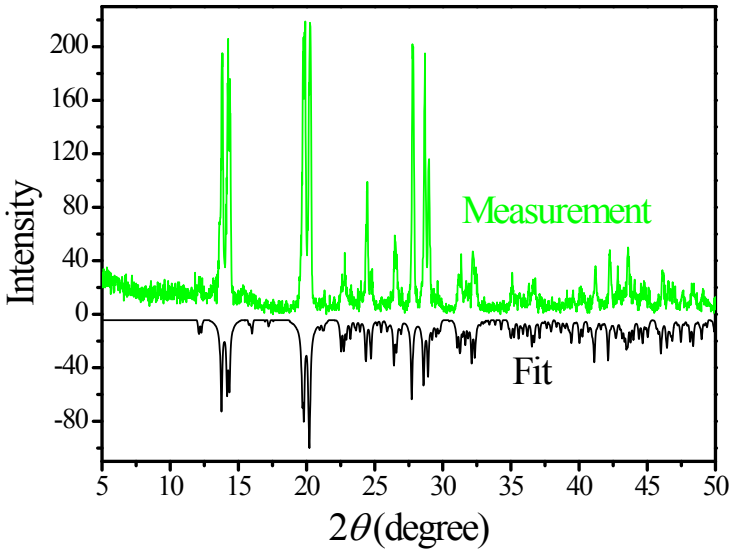

Fig. S3 The PXRD curve for compound 1.

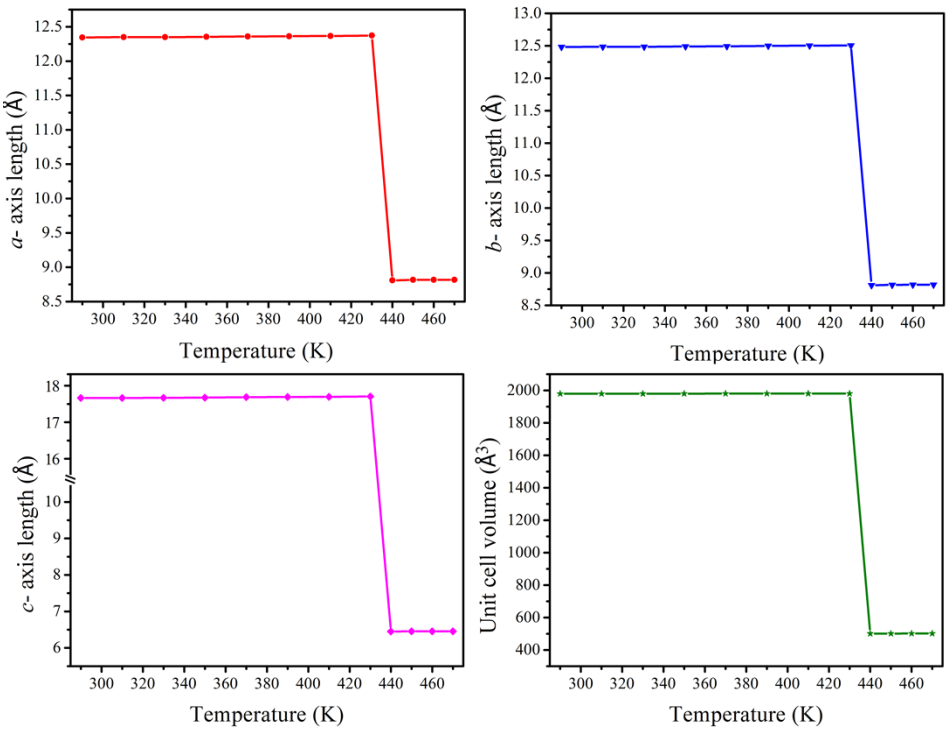

Fig. S4 Temperature- dependent cell parameters of compound 1. Compound 1 shows an obvious negative thermal expansion (NTE) along the *a*, *b*, *c* axes. For the lattice- volume change, the unit- cell volume of the HTP was converted into that of the RTP by dividing by four.

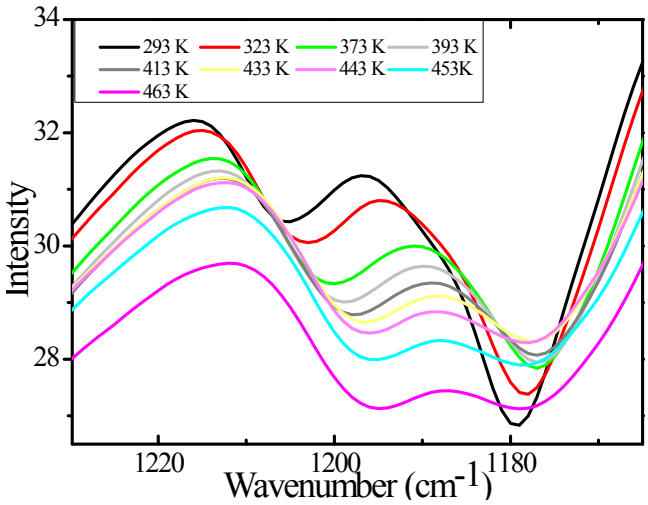

Fig. S5 The intensity of the IR spectra corresponding to the spectral ranges 1060-1230. The changes of the peaks near the 1180 cm^{-1} are aroused by the deformations of the whole ring δ(R) of the imidazolium cations. Besides the intensity of the whole ring increases before the phase transition temperature, while above the phase transition temperature it decreases.

Table S1 Selected bond lengths (Å) and angles (º) for the compound 1

Bond lengths (Å) (RTP)			
Mn(1)-O(6)	2.151(2)	Mn(1)-O(5)	2.158(2)
Mn(1)-O(4)	2.164(2)	Mn(1)-O(1)	2.171(2)
Mn(1)-O(2)	2.186(2)	Mn(1)-O(3)	2.203(2)
Mn(2)-O(12)#1	2.144(2)	Mn(2)-O(10)#2	2.162(2)
Mn(2)-O(9)#3	2.171(2)	Mn(2)-O(8)#4	2.182(2)
Mn(2)-O(11)#5	2.190(2)	Mn(2)-O(7)	2.201(2)
O(8)-Mn(2)#5	2.182(2)	O(11)-Mn(2)#4	2.190(2)
O(9)-Mn(2)#6	2.171(2)	O(12)-Mn(2)#8	2.144(2)
O(10)-Mn(2)#7	2.162(2)		
Bond lengths(Å) (HTP)			
Mn(1)-O(1)#1’	2.163(7)	Mn(1)-O(1)#2’	2.163(7)
Mn(1)-O(1)	2.163(7)	Mn(1)-O(1)#3’	2.163(7)
Mn(1)-O(2)#2’	2.195(13)	Mn(1)-O(2)	2.195(13)
Mn(1)-O(2)#1’	2.195(13)	Mn(1)-O(2)#3’	2.195(13)
Mn(1)-Mn(1)#4’	6.2345(7)	Mn(1)-Mn(1)#5’	6.2345(7)
Mn(1)-Mn(1)#6’	6.2345(7)	Mn(1)-Mn(1)#7’	6.2345(7)
Bond angles (º) (RTP)			
O(6)-Mn(1)-O(5)	90.00(9)	O(6)-Mn(1)-O(4)	91.36(12)
O(5)-Mn(1)-O(4)	92.18(9)	O(6)-Mn(1)-O(1)	93.33(11)
O(5)-Mn(1)-O(1)	94.27(10)	O(4)-Mn(1)-O(1)	172.02(10)
O(6)-Mn(1)-O(2)	90.02(9)	O(5)-Mn(1)-O(2)	179.06(9)
O(4)-Mn(1)-O(2)	86.88(9)	O(1)-Mn(1)-O(2)	86.67(10)
O(6)-Mn(1)-O(3)	177.96(8)	O(5)-Mn(1)-O(3)	91.46(8)
O(4)-Mn(1)-O(3)	87.16(11)	O(1)-Mn(1)-O(3)	87.98(10)
O(2)-Mn(1)-O(3)	88.49(9)	O(12)#1-Mn(2)-O(10)#2	97.10(10)
O(12)#1-Mn(2)-O(9)#3	172.01(8)	O(10)#2-Mn(2)-O(9)#3	90.86(10)
O(12)#1-Mn(2)-O(8)#4	89.01(9)	O(10)#2-Mn(2)-O(8)#4	96.38(9)
O(9)#3-Mn(2)-O(8)#4	89.36(9)	O(12)#1-Mn(2)-O(11)#5	90.99(9)
O(10)#2-Mn(2)-O(11)#5	81.76(9)	O(9)#3-Mn(2)-O(11)#5	90.89(9)
O(8)#4-Mn(2)-O(11)#5	178.13(8)	O(12)#1-Mn(2)-O(7)	82.33(10)
O(10)#2-Mn(2)-O(7)	173.16(9)	O(9)#3-Mn(2)-O(7)	89.86(9)
O(8)#4-Mn(2)-O(7)	90.43(9)	O(11)#5-Mn(2)-O(7)	91.42(9)
C(1)-O(1)-Mn(1)	140.4(2)	C(2)-O(2)-Mn(1)	136.0(2)
C(3)-O(3)-Mn(1)	128.6(2)	C(4)-O(4)-Mn(1)	141.6(2)
C(5)-O(5)-Mn(1)	130.9(2)	C(6)-O(6)-Mn(1)	133.9(2)
C(1)-O(7)-Mn(2)	139.9(2)	C(2)-O(8)-Mn(2)#5	129.9(2)
C(3)-O(9)-Mn(2)#6	128.8(2)	C(4)-O(10)-Mn(2)#7	143.3(2)
C(5)-O(11)-Mn(2)#4	133.8(2)	C(6)-O(12)-Mn(2)#8	134.6(2)
Bond angles (º) (HTP)			
O(1)#1-Mn(1)-O(1)#2’	178.3(7)	O(1)#1-Mn(1)-O(1)	90.013(11)

O(1)#2-Mn(1)-O(1)	90.013(12)	O(1)#1-Mn(1)-O(1)#3’	90.013(12)
O(1)#2-Mn(1)-O(1)#3’	90.013(12)	O(1)-Mn(1)-O(1)#3’	178.3(7)
O(1)#1-Mn(1)-O(2)#2’	95.4(14)	O(1)#2-Mn(1)-O(2)#2’	83.0(13)
O(1)-Mn(1)-O(2)#2’	97.1(10)	O(1)#3-Mn(1)-O(2)#2’	84.6(10)
O(1)#1-Mn(1)-O(2)	97.1(10)	O(1)#2-Mn(1)-O(2)	84.6(10)
O(1)-Mn(1)-O(2)	83.0(13)	O(1)#3-Mn(1)-O(2)	95.4(14)
O(2)#2-Mn(1)-O(2)	167.6(6)	O(1)#1-Mn(1)-O(2)#1’	83.0(13)
O(1)#2-Mn(1)-O(2)#1’	95.4(14)	O(1)-Mn(1)-O(2)#1’	84.6(10)
O(1)#3-Mn(1)-O(2)#1’	97.1(10)	O(2)#2-Mn(1)-O(2)#1’	17.6(9)
O(2)-Mn(1)-O(2)#1’	167.6(6)	O(1)#1-Mn(1)-O(2)#3’	84.6(10)
O(1)#2-Mn(1)-O(2)#3’	97.1(10)	O(1)-Mn(1)-O(2)#3’	95.4(14)
O(1)#3-Mn(1)-O(2)#3’	83.0(13)	O(2)#2-Mn(1)-O(2)#3’	167.6(6)
O(2)-Mn(1)-O(2)#3’	17.6(9)	O(2)#1-Mn(1)-O(2)#3’	167.6(6)
O(1)#1-Mn(1)-Mn(1)#4’	159.51(16)	O(1)#2-Mn(1)-Mn(1)#4’	20.49(16)
O(1)-Mn(1)-Mn(1)#4’	110.47(17)	O(1)#3-Mn(1)-Mn(1)#4’	69.53(17)
O(2)#2-Mn(1)-Mn(1)#4’	82.0(9)	O(2)-Mn(1)-Mn(1)#4’	86.3(13)
O(2)#1-Mn(1)-Mn(1)#4’	98.0(9)	O(2)#3-Mn(1)-Mn(1)#4’	93.7(13)
O(1)#1-Mn(1)-Mn(1)#5’	20.49(16)	O(1)#2-Mn(1)-Mn(1)#5’	159.51(16)
O(1)-Mn(1)-Mn(1)#5’	69.53(17)	O(1)#3-Mn(1)-Mn(1)#5’	110.47(17)
O(2)#2-Mn(1)-Mn(1)#5’	98.0(9)	O(2)-Mn(1)-Mn(1)#5’	93.7(13)
O(2)#1-Mn(1)-Mn(1)#5’	82.0(9)	O(2)#3-Mn(1)-Mn(1)#5’	86.3(13)
Mn(1)#4-Mn(1)-Mn(1)#5’	180.0	O(1)#1-Mn(1)-Mn(1)#6’	110.47(17)
O(1)#2-Mn(1)-Mn(1)#6’	69.53(17)	O(1)-Mn(1)-Mn(1)#6’	20.49(16)
O(1)#3-Mn(1)-Mn(1)#6’	159.51(16)	O(2)#2-Mn(1)-Mn(1)#6’	93.7(13)
O(2)-Mn(1)-Mn(1)#6’	82.0(9)	O(2)#1-Mn(1)-Mn(1)#6’	86.3(13)
O(2)#3-Mn(1)-Mn(1)#6’	98.0(9)	Mn(1)#4-Mn(1)-Mn(1)#6’	90.0
Mn(1)#5-Mn(1)-Mn(1)#6’	90.0	O(1)#1-Mn(1)-Mn(1)#7’	69.53(17)
O(1)#2-Mn(1)-Mn(1)#7’	110.47(17)	O(1)-Mn(1)-Mn(1)#7’	159.51(16)
O(1)#3-Mn(1)-Mn(1)#7’	20.49(16)	O(2)#2-Mn(1)-Mn(1)#7’	86.3(13)
O(2)-Mn(1)-Mn(1)#7’	98.0(9)	O(2)#1-Mn(1)-Mn(1)#7’	93.7(13)
O(2)#3-Mn(1)-Mn(1)#7’	82.0(9)	Mn(1)#4-Mn(1)-Mn(1)#7’	90.0
Mn(1)#5-Mn(1)-Mn(1)#7’	90.0	Mn(1)#6-Mn(1)-Mn(1)#7’	180.0

#1 x-1,-y+1/2,z-1/2 #2 x-1,y,z-1 #3 x,-y+1/2,z-1/2 #4 -x+1,y+1/2,-z+1/2
#5 -x+1,y-1/2,-z+1/2 #6 x,-y+1/2,z+1/2 #7 x+1,y,z+1 #8 x+1,-y+1/2,z+1/2
#1’ y,-x+1,-z+1 #2’ -y+1,x,-z+1 #3’ -x+1,-y+1,z #4’ -x+3/2,y+1/2,-z+1
#5’ -x+1/2,y-1/2,-z+1 #6’ -x+3/2,y-1/2,-z+1 #7’ -x+1/2,y+1/2,-z+1

Table S2 Hydrogen bonds for compound 1 at different temperatures [Å and deg.]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
RTP				
N(1)-H(1A)...O(8)#6	0.86	1.95	2.792(4)	167.5
N(1)-H(1A)...O(2)#6	0.86	2.61	3.138(4)	120.4

N(4)-H(4A)…O(3)#9	0.86	1.94	2.803(4)	178.0
N(4)-H(4A)...O(9)#9	0.86	2.63	3.211(4)	126.3
N(2)-H(2A)...O(11)	0.97(5)	1.87(5)	2.829(4)	172(4)
N(3)-H(3A)...O(7)#10	0.96(6)	1.89(6)	2.851(4)	173(5)
N(3)-H(3A)...O(1)#10	0.96(6)	2.54(5)	3.180(4)	124(4)
HTP				
N2-H2A...O1#1	0.90	2.25	2.96(3)	134.8
N2-H2A...O2#1	0.90	2.44	3.25(6)	149.4
N1-H1A…O1#3	0.90	2.24	3.10(3)	158.6
N1-H1A…O1#4	0.90	2.51	3.26(3)	141.4

Symmetry transformations used to generate equivalent atoms: #6 x, -y+1/2, z+1/2 #9 x, y+1, z

#10 -x+1,-y+1,-z+1 #1 y+1/2, x-1/2, z #3 -y+1/2, -x+1/2, z+1 #4 -x+1, -y, z+1