SSupporting Information for

Novel pure Pnma-$P2_12_12_1$ ferroelastic phase transition of 1,4-diisopropyl-1,4-diazonia-bicyclo[2.2.2]octane tetra-chlorobromo-M(II) (M=Mn and Co)

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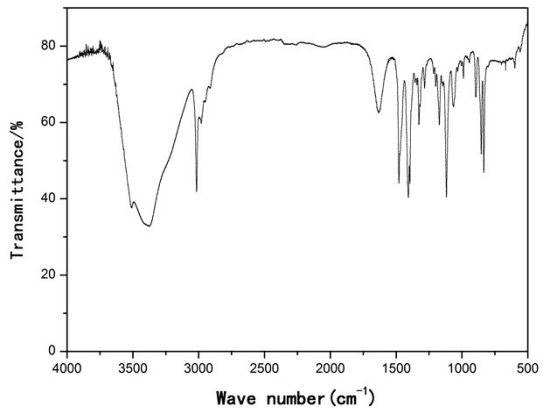

Figure S1 IR of **1**

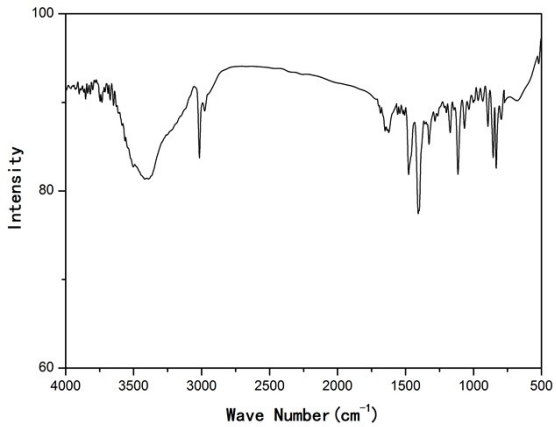

Figure S1 IR of **2**

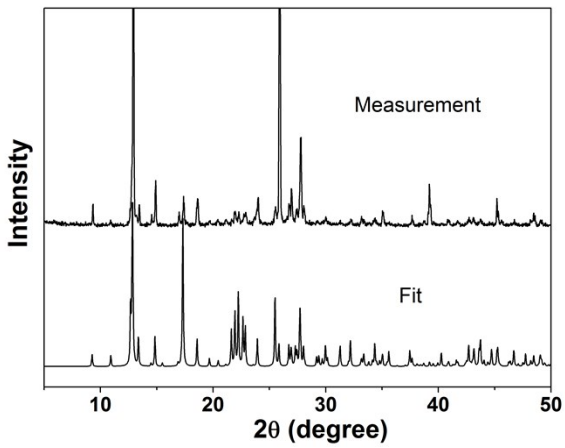

Figure S3 XRPD pattern of **1**, where the lower line is the simulated pattern.

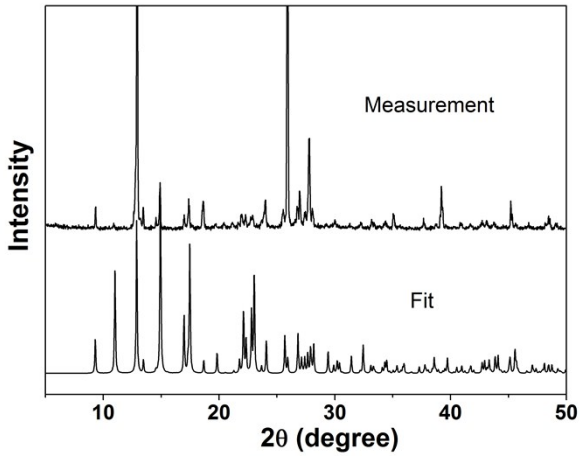

Figure S4 XRPD pattern of **2**, where the lower line is the simulated pattern.

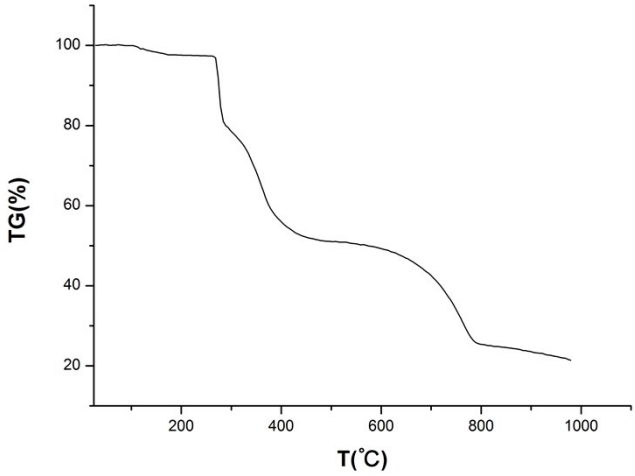

Figure S5 TG curve of **1**

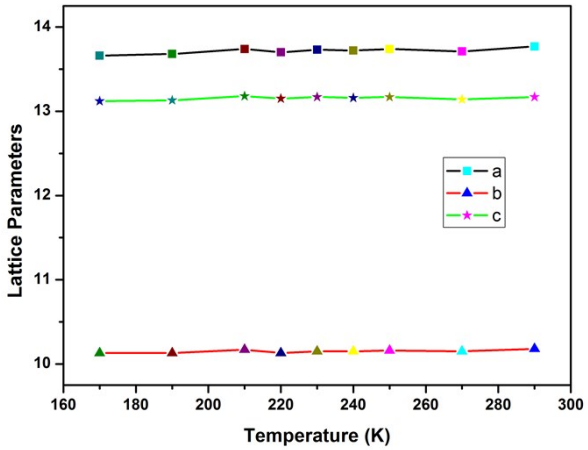

Figure S6 Temperature dependence of unit-cell lengths parameters of **2**

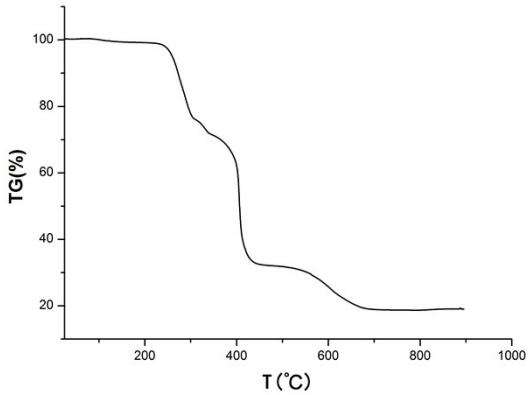

Figure S7 TG curve of **2**

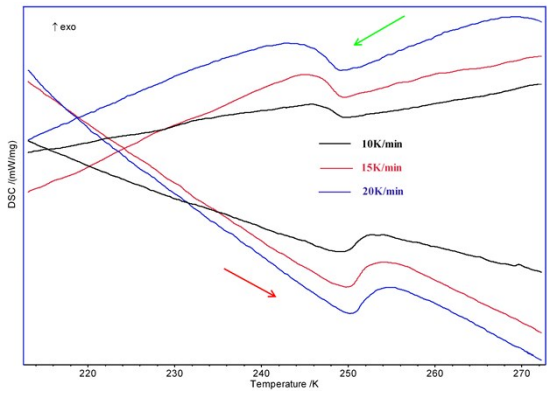

Figure S8 DSC curves of **1** obtained in a heating-cooling mode at 10 K/min, 15 K/min and 20 K/min respectively.

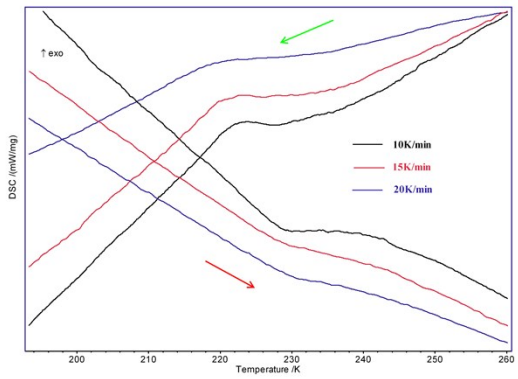

Figure S9 DSC curves of **2** obtained in a heating-cooling mode at 10 K/min, 15 K/min and 20 K/min respectively.

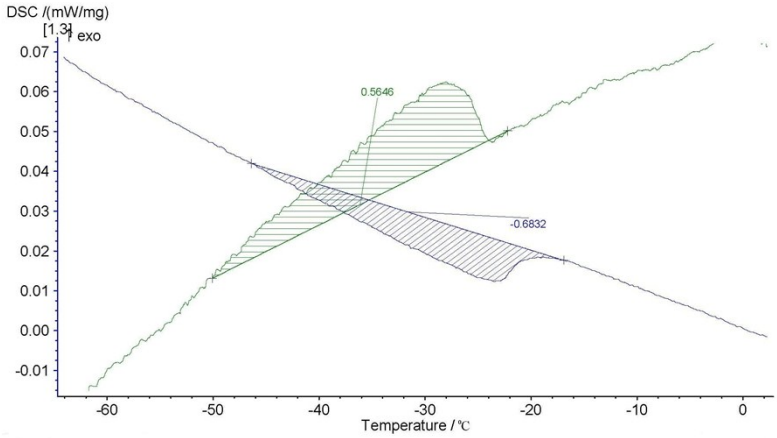

Figure S10 The enthalpy changes (ΔH) of **1** obtained in a heating-cooling mode at 15 K/min.

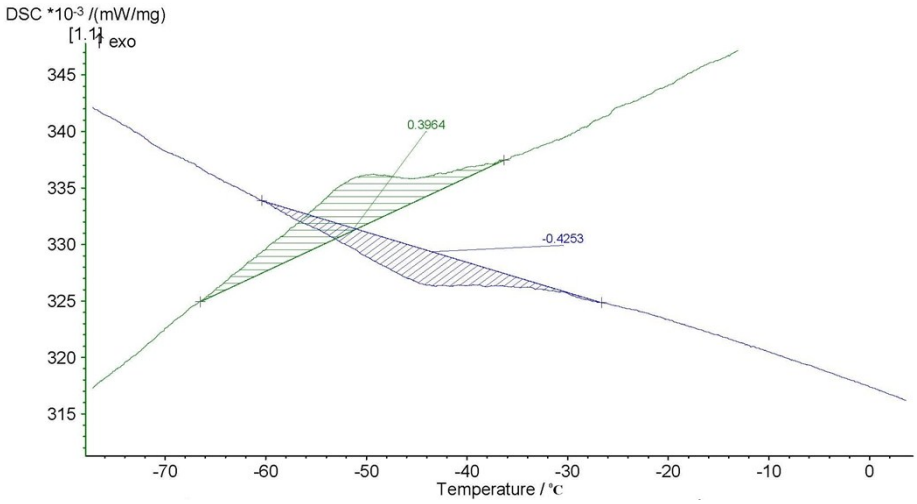

Figure S11 The enthalpy changes (ΔH) of **2** obtained in a heating-cooling mode at 10 K/min.

Table S1 Selected Bond Lengths (Å) and Bond Angles (°) (296 K) of **1**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Mn(1)-Cl(3)	2.332(12)	Mn(1)-Cl(2)	2.3706(10)	Mn(1)-Cl(1)	2.459(18)
Mn(1)-Cl(2)#1	2.3706(10)	Mn(1)-Br(1)	2.452(3)	Mn(1)-Br(3)	2.462(12)
Angle	(°)	Angle	(°)	Angle	(°)
Cl(3)-Mn(1)-Cl(2)#1	108.37(11)	Cl(2)-Mn(1)-Br(1)	113.87(5)	Cl(3)-Mn(1)-Br(3)	2.5(3)
Cl(3)-Mn(1)-Cl(2)	108.37(11)	Cl(3)-Mn(1)-Cl(1)	101.3(3)	Cl(2)#1-Mn(1)-Br(3)	106.99(10)
Cl(2)#1-Mn(1)-Cl(2)	105.05(6)	Cl(2)#1-Mn(1)-Cl(1)	116.67(12)	Cl(2)-Mn(1)-Br(3)	106.99(10)
Cl(3)-Mn(1)-Br(1)	107.1(2)	Cl(2)-Mn(1)-Cl(1)	116.67(12)	Br(1)-Mn(1)-Br(3)	109.60(18)
Cl(2)#1-Mn(1)-Br(1)	113.87(5)	Br(1)-Mn(1)-Cl(1)	5.8(3)	Cl(1)-Mn(1)-Br(3)	103.8(3)

Symmetry transformation: #1: x,-y+3/2,z

Table S2 Selected Bond Lengths (Å) and Bond Angles (°) (150 K) of **1**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Mn(1)-Cl(3)	2.3536(10)	Mn(1)-Cl(2)	2.3909(8)	Mn(1)-Cl(4)	2.448(13)
Mn(1)-Cl(1)	2.390(5)	Mn(1)-Br(1)	2.436(4)	Mn(1)-Br(4)	2.476(2)
Angle	(°)	Angle	(°)	Angle	(°)
Cl(3)-Mn(1)-Cl(1)	110.57(15)	Cl(2)-Mn(1)-Br(1)	103.51(9)	Cl(3)-Mn(1)-Br(4)	110.53(6)
Cl(3)-Mn(1)-Cl(2)	106.29(3)	Cl(3)-Mn(1)-Cl(4)	113.7(4)	Cl(1)-Mn(1)-Br(4)	108.98(12)
Cl(1)-Mn(1)-Cl(2)	103.99(14)	Cl(1)-Mn(1)-Cl(4)	103.7(2)	Cl(2)-Mn(1)-Br(4)	116.26(6)
Cl(3)-Mn(1)-Br(1)	110.49(9)	Cl(2)-Mn(1)-Cl(4)	118.1(4)	Br(1)-Mn(1)-Br(4)	109.50(8)
Cl(1)-Mn(1)-Br(1)	0.57(18)	Br(1)-Mn(1)-Cl(4)	104.2(2)	Cl(4)-Mn(1)-Br(4)	5.3(3)

Table S3 Selected Bond Lengths (Å) and Bond Angles (°) (296 K) of **2**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Co(1) -Cl(1)	2.2855(13)	Co(1) -Br(2)	2.3733(15)	Cl(1)#1-Co(1)	2.2855(13)
Co(1) -Cl(3)	2.26(2)	Co(1) -Br(3)	2.39(3)		
Angle	(°)	Angle	(°)	Angle	(°)
Cl(3)-Co(1)-Cl(1)	109.8(3)	Cl(3)-Co(1)-Br(2)	105.1(5)	Cl(3)-Co(1)-Br(3)	4.8(11)
Cl(3)-Co(1)-Cl(1)#1	109.8(3)	Cl(1)-Co(1)-Br(2)	113.81(5)	Cl(1)-Co(1)-Br(3)	107.2(3)
Cl(1)-Co(1)-Cl(1)#1	104.55(8)	Cl(1)#1-Co(1)-Br(2)	113.81(5)	Cl(1)#1-Co(1)-Br(3)	107.2(3)
Br(2)-Co(1)-Br(3)	109.9(6)				

Symmetry transformation: #1: x,-y+1/2,z

Table S4 Selected Bond Lengths (Å) and Bond Angles (°) (150 K) of **2**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Co(1)-Cl(1)	2.2734(14)	Co(1)-Br(3)	2.3926(8)	Co(1)-Br(4)	2.341(14)
Co(1)-Cl(2)	2.3048(12)	Co(1)-Cl(4)	2.323(12)		
Angle	(°)	Angle	(°)	Angle	(°)
Cl(1)-Co(1)-Cl(2)	105.71(5)	Cl(1)-Co(1)-Br(4)	109.9(3)	Cl(1)-Co(1)-Br(3)	110.40(5)
Cl(1)-Co(1)-Cl(4)	111.0(3)	Cl(2)-Co(1)-Br(4)	105.5(3)	Cl(2)-Co(1)-Br(3)	116.23(4)

Cl(2)-Co(1)-Cl(4)	105.0(3)	Cl(4)-Co(1)-Br(4)	1.1(6)	Cl(4)-Co(1)-Br(3)	108.4(3)
Br(4)-Co(1)-Br(3)	108.9(3)				