Electronic Supplementary Information

Two-step nonlinear optical switch in a hydrogen-bonded perovskite-type crystal

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Synthesis. Rod-like pink crystals of $[C_4H_{12}NO]MnCl_3$ (compound **1**) were obtained from the evaporation of concentrated HCl solution (36%, w/w) containing stoichiometric amounts of N,N-dimethylethanolamine and $MnCl_2{\cdot}4H_2O$ after several weeks. The phase purity of compound **1** was validated by IR and powder X-ray diffraction (PXRD) measurements (Figs. S1 and S2).

Single crystal X-ray diffraction. Suitable crystals were selected for structural determination. X-ray diffraction data were collected at 223, 293 and 393 K with Mo Kα radiation (λ = 0.71073 Å) through a Rigaku Saturn 924 CCD diffractometer. The crystal structures at various temperatures were solved by direct methods and refined by the full-matrix methods based on F^2, employing SHELXTL-2014 software package. And the crystallographic data of compound **1** at 223 K was executed with a twin data reduction and refinement. Non-H atoms were refined anisotropically and H atoms were positioned geometrically. The relationship of the cells in the three crystal structures is *a* (223 K) ≈ *b* (293 K) ≈ *c* (393 K), *b* (223 K) ≈ *c* (293 K) ≈ *a* (393 K), and *c* (223 K) ≈ *a* (293 K) ≈ *b* (393 K).

Powder X-ray diffraction (PXRD) measurements. Rigaku Smartlab Powder X-Ray Diffractometer was used to check the phase purity of desired compound. The experimental PXRD patterns were recorded in the 2ϑ range of 5°-45° with a step size of 5°/min. The experimental PXRD patterns obtained at 223, 293 and 393 K match well with the calculated data based on the corresponding single-crystal structures (Fig. S2), which solidly confirm the purity of the as-grown crystals and the structural phase transitions of compound **1**.

Differential scanning calorimetry (DSC) and dielectric measurements. DSC measurements of compound **1** were performed on the polycrystalline samples that were placed in aluminum crucibles using a NETZSCH DSC 200 F3 instrument within the temperature range of 220-300 K and 350-400 K under a nitrogen atmosphere with a heating/cooling rate of 10 K min^{-1}. The exploration of dielectric properties was carried out on a Tonghui TH2828A apparatus upon pressed-powder pellets which were deposited as the electrodes.

Second-harmonic generation (SHG) activity measurements. Variable-temperature SHG

experiments were carried out on the polycrystalline samples of compound **1** at a sweeping rate of 10 K min^{-1}, using an unexpanded laser beam with low divergence (pumped by an Nd:YAG laser with 1064 nm, 5 ns pulse duration, 10 Hz repetition rate) as fundamental beam. The instrument model is Ins 1210058, INSTEC Instruments. And the laser was Vibrant 355 II instrument from OPOTEK. The numerical values of the nonlinear optical coefficient for SHG have been determined by comparing with KH_2PO_4 (KDP) as the reference standard.

Ultraviolet-visible (UV-vis) absorption and fluorescence spectrometry. UV-Vis measurement of compound **1** was documented in a Shimadzu UV-2600 spectrophotometer with an ISR-2600Plus integrating sphere functioning from 200 to 900 nm, using $BaSO_4$ as the 100% reflectance reference. The emission and excitation spectra were collected on an Edinburgh FLS-920 fluorescence spectrometer based on the solid states.

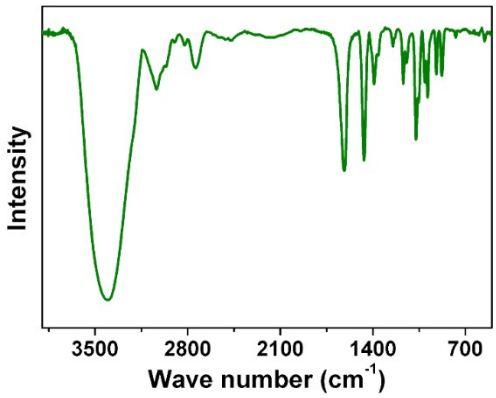

Fig. S1 IR spectrum of compound **1** at 293 K.

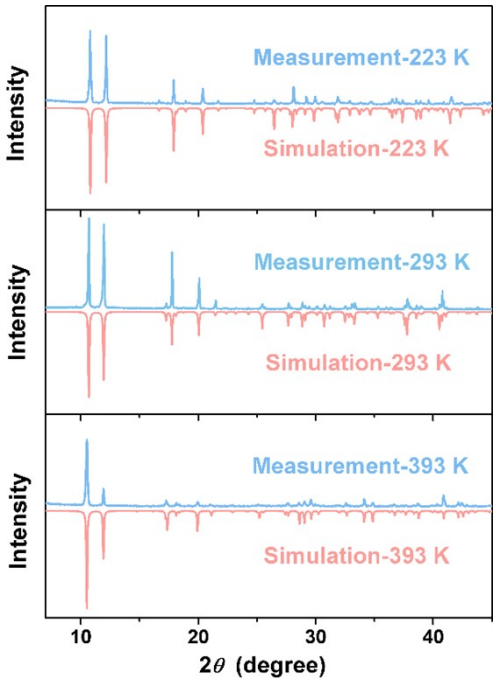

Fig. S2 The measured PXRD patterns of compound **1** match well with the simulated ones based on the corresponding crystals structure at 223, 293 and 393 K.

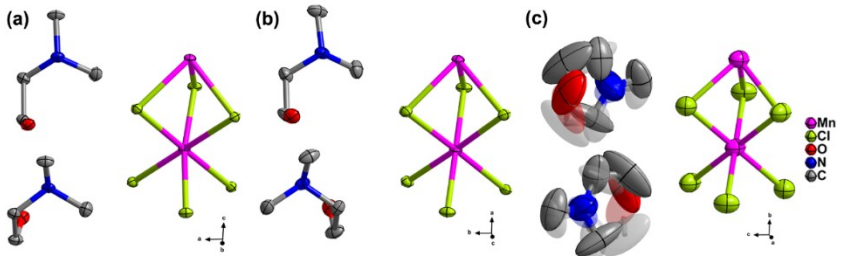

Fig. S3 Representative ORTEP diagram of compound **1** at (a) 223 K, (b) 239 K and (c) 393 K. Thermal ellipsoids are set at 30% probability level. All the hydrogen atoms are omitted for clarity.

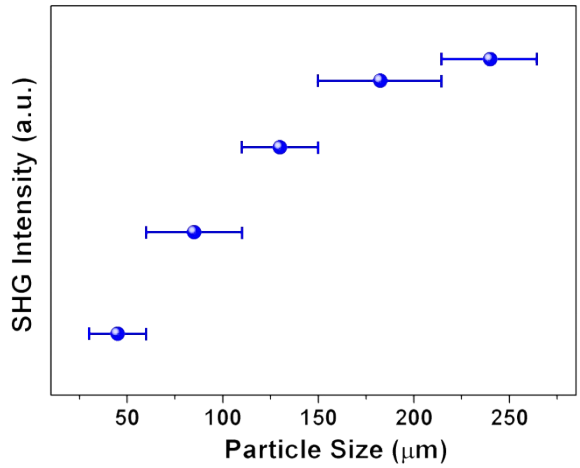

Fig. S4 SHG intensity of compound **1** plotted against particle size.

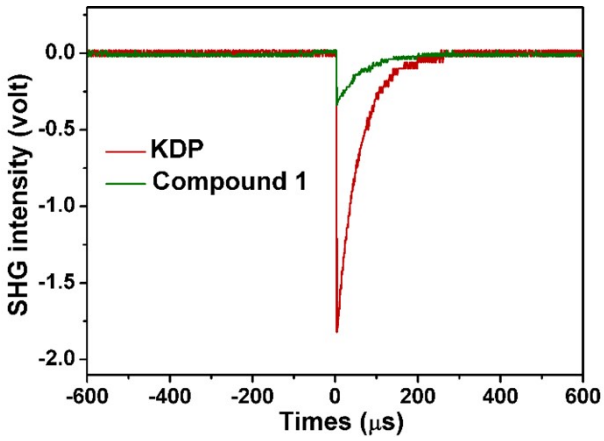

Fig. S5 SHG signal of compound **1** and KDP at the grain size of 210-260 μm at 293 K.

Table S1 Crystal data and structure refinement details for compound **1**.

Empirical formula		$[C_4H_{12}NO]MnCl_3$	
Formula		251.44	
T (K)	223	293	393
Crystal system	Monoclinic	Orthorhombic	Orthorhombic

Space group	$P2_1/c$	$P2_12_12_1$	$Pnma$
a/Å	9.9332(9)	6.5395(2)	14.837(2)
b/Å	14.5412(11)	9.9821(3)	6.5021(10)
c/Å	6.5977(6)	14.8082(5)	10.2026(15)
β (deg)	95.019(8)	90	90
V/Å^3	949.32(14)	966.65(5)	984.3(2)
Z	4	4	4
F(000)	508.0	508.0	508.0
Unique reflections	1663	1691	1056
Parameters refined	94	94	80
GOF	1.277	1.148	1.096
R_1	0.0496	0.0140	0.0442
wR_2	0.1395	0.0379	0.1194

Table S2 Selected bond lengths [Å] and angles [°] for compound **1** at 223 K.

223 K	Mn1-Cl3	2.5252(15)	Mn1-Cl2#1	2.5496(16)
	Mn1-Cl3#1	2.5473(15)	Mn1-Cl2	2.5655(16)
	Mn1-Cl1#1	2.5967(15)	Mn1-Cl1	2.6112(15)
	Cl3-Mn1-Cl3#1	170.82(8)	Cl3-Mn1-Cl2#1	100.92(5)
	Cl3#1-Mn1-Cl2#1	85.07(5)	Cl3-Mn1-Cl2	85.20(5)
	Cl3#1-Mn1-Cl2	101.17(5)	Cl2#1-Mn1-Cl2	96.26(6)
	Cl3-Mn1-Cl1#1	91.91(5)	Cl3#1-Mn1-Cl1#1	81.93(5)
	Cl2#1-Mn1-Cl1#1	82.33(5)	Cl2-Mn1-Cl1#1	176.49(6)
	Cl3-Mn1-Cl1	82.07(5)	Cl3#1-Mn1-Cl1	92.24(5)
	Cl2#1-Mn1-Cl1	176.29(6)	Cl2-Mn1-Cl1	81.74(5)
	Cl1#1-Mn1-Cl	99.84(6)		
Symmetry codes: #1 x, -y+1/2, z+1/2.				

Table S3 Selected bond lengths [Å] and angles [°] for compound **1** at 293 K.

293K	Mn1-Cl1#1	2.5285(6)	Mn1-Cl2#1	2.5429(6)
	Mn1-Cl2	2.5571(6)	Mn1-Cl3	2.5589(6)
	Mn1-Cl1	2.5606(6)	Mn1-Cl3#1	2.6261(6)
	Cl1#1-Mn1-Cl2#1	84.919(19)	Cl1#1-Mn1-Cl2	95.09(2)
	Cl2#1-Mn1-Cl2	179.83(2)	Cl1#1-Mn1-Cl3	95.64(2)
	Cl2#1-Mn1-Cl3	96.05(2)	Cl2-Mn1-Cl3	83.779(18)
	Cl1#1-Mn1-Cl1	178.83(2)	Cl2#1-Mn1-Cl1	96.02(2)
	Cl2-Mn1-Cl1	83.976(18)	Cl3-Mn1-Cl1	83.566(19)
	Cl1#1-Mn1-Cl3#1	82.849(18)	Cl2#1-Mn1-Cl3#1	82.715(17)
	Cl2-Mn1-Cl3#1	97.458(19)	Cl3-Mn1-Cl3#1	178.12(2)
	Cl1-Mn1-Cl3#1	97.96(2)		
Symmetry codes: #1 x+1/2, -y+3/2, -z+2.				

Table S4 Selected bond lengths [Å] and angles [°] for compound **1** at 393 K.

393K	Mn1-Cl3#1	2.5395(12)	Mn1-Cl3	2.5395(12)
	Mn1-Cl2#1	2.5598(12)	Mn1-Cl2	2.5598(12)
	Mn1-Cl1	2.5630(13)	Mn1-Cl1#1	2.5631(13)
	Cl3#1-Mn1-Cl3	180.0	Cl3#1-Mn1-Cl2#1	95.82(5)
	Cl3-Mn1-Cl2#1	84.18(5)	Cl3#1-Mn1-Cl2	84.18(5)
	Cl3-Mn1-Cl2	95.82(5)	Cl2#1-Mn1-Cl2	180.00(6)
	Cl3#1-Mn1-Cl1	83.72(5)	Cl3-Mn1-Cl1	96.28(5)
	Cl2#1-Mn1-Cl1	96.44(5)	Cl2-Mn1-Cl1	83.56(5)
	Cl3#1-Mn1-Cl1#1	96.28(5)	Cl3-Mn1-Cl1#1	83.72(5)
	Cl2#1-Mn1-Cl1#1	83.56(5)	Cl2-Mn1-Cl1#1	96.44(5)
	Cl1-Mn1-Cl1#1	180.0		
Symmetry codes: #1 -x+1, -y+1, -z+1.				

Table S5 Hydrogen bond geometry (Å, degree) at 223 K in compound **1**.

	D-H···A	H···A[Å]	D···A[Å]	D-H···A [°]
223 K	O1-H1···Cl1#5	2.27	3.089(5)	172.3
	N1-H1D···O1#2	1.98	2.862(6)	146.9
Symmetry codes: #2 x, -y+1/2, z-1/2; #5 x-1, y, z.				

Table S6 Hydrogen bond geometry (Å, degree) at 293 K in compound **1**.

	D-H···A	H···A[Å]	D···A[Å]	D-H···A [°]
293 K	O1-H1···Cl3#3	2.34	3.133(2)	163.3
	N1-H1D···O1#4	2.03	2.919(2)	150.3
Symmetry codes: #3 -x+3/2, -y+2, z-1/2; #4 x-1/2, -y+3/2, -z+1.				