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Supplement information

Room temperature ferroelectric material with photoluminescence: (1,3-Dicyclohexylimidazole)$_2$MnCl$_4$

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EXPERIMENTAL SECTION

Synthesis. All reagents used in this article were analytical reagents and without further purification.

0.562 g (2mmol, purity 97 %, Aldrich) of 1,3-Dicyclohexylimidazole hydrochloride（$C_{15}H_{29}ClN_2$） and 0.127 g (1mmol, purity 99 %, Aldrich) of manganese chloride（$MnCl_2$） were dissolved by deionized water in a beaker, and a few hydrochloric acid (purity 37 %, Aldrich) was added to the mixed solution to ensure an acidic environment of the solution. Cover the mouth of the beaker with a perforated anti-corrosion film to limit the evaporation rate of the solution, and let the beaker stand at room temperature to evaporate slowly. Green transparent flake crystals were obtained after about 2 weeks.

DSC Measurements. Differential scanning calorimetry was performed on a PerkinElmer Diamond DSC instrument in the temperature range 173~373 K under an atmosphere of nitrogen in aluminium crucibles with a heating rate of 10 K/min.

Structure stability

The single crystal sample is grinded and sieved into polycrystalline powder(particle size is 100~150 μm） for SHG measurement. Using a low-divergence non-expanding laser beam (pulsed Nd: YAG, wavelength 1064 nm, pulse duration 5 ns, peak power 1.6 MW, repetition frequency 10c Hz). FLS 920 from Edinburgh Instruments was used as the instrument model, and the temperature was 290~400 K with a cooling and heating rate of 2 K/min with the DE 202 system, while the laser was Vibrant 355 II instrument

from the OPOTEK system. Numerical values for the nonlinear optical coefficients for the SHG were determined by comparison to a KDP benchmark.

Electrical property measurements

The dielectric anomaly, pyroelectric and ferroelectric hysteresis loops were measured by using the upper and lower silver plating layers of (1,3-Dicyclohexylimidazole)$_2$MnCl$_4$ crystal slice as electrodes. The temperature dependence of the complex permittivity at 500 Hz to 1 MHz was measured using Tonghui TH2828A LCR meter. The pyroelectric current of variable temperature is also measured on the electrometer (Keithley 6517B). The ferroelectric hysteresis loop is measured in the radiation RT6000 Premier II tester. The ferroelectric hysteresis loops are measured in the radiation RT6000 Premier II tester using the Sawyer-Tower method and in the electrometer (Keithley 6517B) using the double-wave method (DWM), respectively.

Structural characterization

Single crystal X-ray diffraction experiments were carried out at different temperatures using a Rigaku Saturn 924 diffractometer with Mo-Kα radiation (λ = 0.71073 Å).

Photoluminescence measurements

Using BWPL-1000 variable temperature photoluminescence (PL) test system to test PL spectral lines of crystals in the range of 273 K to 373 K.

Table S1. Crystal data and structure refinements for **DHIMC** at various temperatures.

Temperature	278K	338K
Chemical formula	$C_{119.5}H_{203}C_{116}Mn_4N_{16}$	$C_{103}H_{179}C_{116}Mn_4N_{16}$
Crystallographic system	Triclinic	Triclinic
Space group	P1	$\overline{P}$
Cell parameters(Å)	16.9646(7)	16.9646(7)
	17.3879(7)	17.3879(7)
	26.9590(11)	26.9590(11)
Volume(Å^3)	7177.4(5)	7177.4(5)
Z	2	2
F(000)	2813.0	2562.0
Reflections collected	117164	117157
Independent reflections	46490	25136
parameters	2765	1252
GOF	1.035	1.068
R_1	0.0964	0.1022
wR_2	0.2442	0.2859

Figure S1. The structure diagram of the inorganic component of **DHIMC** at HTP.

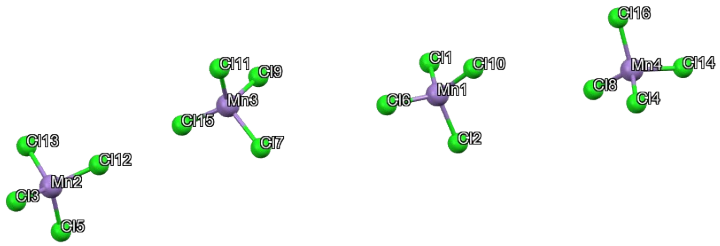


Table S2. The geometric details of the inorganic component of **DHIMC** at HTP.

Number	Atom1	Atom2	Length
1	**Mn1**	**Cl1**	**2.388(2)**
2	**Mn1**	**Cl6**	**2.371(3)**
3	**Mn1**	**Cl10**	**2.349(2)**
4	**Mn1**	**Cl2**	**2.355(3)**
5	**Mn4**	**Cl4**	**2.373(2)**
6	**Mn4**	**Cl8**	**2.361(2)**
7	**Mn4**	**Cl14**	**2.365(3)**
8	**Mn4**	**Cl16**	**2.375(2)**

9	**Mn2**	**Cl12**	**2.365(2)**
10	**Mn2**	**Cl5**	**2.347(4)**
11	**Mn2**	**Cl3**	**2.381(4)**
12	**Mn2**	**Cl13**	**2.364(4)**
13	**Mn3**	**Cl9**	**2.376(3)**
14	**Mn3**	**Cl11**	**2.382(4)**
15	**Mn3**	**Cl7**	**2.376(5)**
16	**Mn3**	**Cl15**	**2.332(5)**

Figure S2. The structure diagram of the inorganic component of **DHIMC** at LTP.

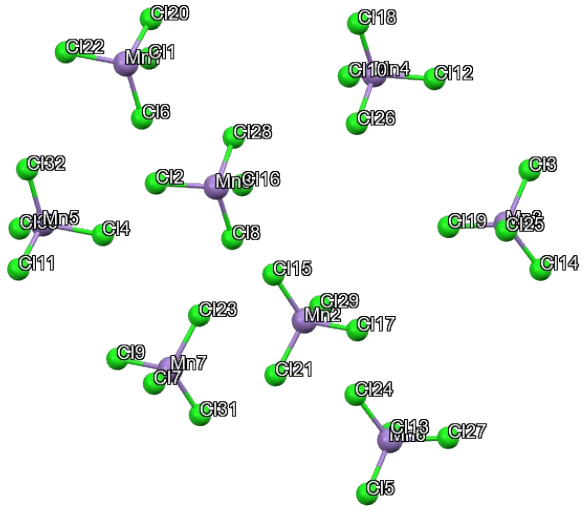


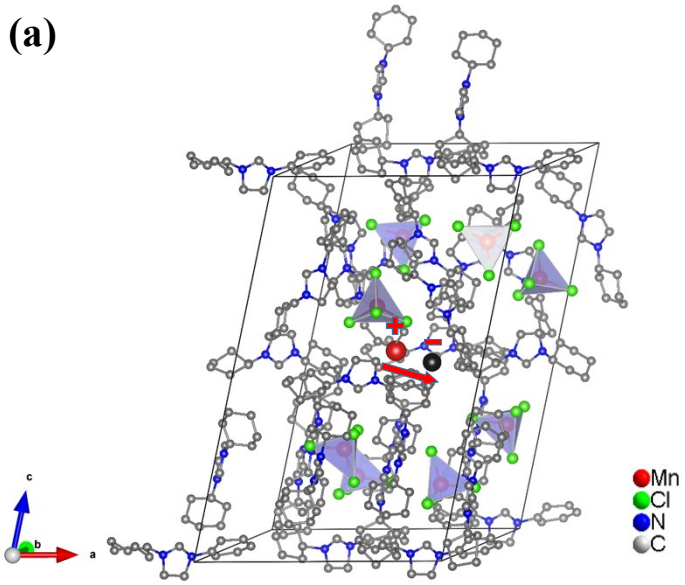
Table S3. The geometric details of the inorganic component of **DHIMC** at LTP.

Number	Atom1	Atom2	Length
1	**Mn1**	**Cl1**	**2.392(5)**
2	**Mn1**	**Cl6**	**2.362(6)**
3	**Mn1**	**Cl20**	**2.344(8)**
4	**Mn1**	**Cl22**	**2.369(8)**
5	**Mn2**	**Cl15**	**2.35(1)**
6	**Mn2**	**Cl17**	**2.363(9)**
7	**Mn2**	**Cl21**	**2.38(1)**
8	**Mn2**	**Cl29**	**2.37(1)**
9	**Mn3**	**Cl3**	**2.351(9)**
10	**Mn3**	**Cl14**	**2.364(7)**
11	**Mn3**	**Cl19**	**2.37(1)**
12	**Mn3**	**Cl25**	**2.367(9)**
13	**Mn4**	**Cl10**	**2.369(5)**
14	**Mn4**	**Cl12**	**2.364(9)**
15	**Mn4**	**Cl18**	**2.346(6)**

16	**Mn4**	**Cl26**	**2.384(7)**
17	**Cl4**	**Mn5**	**2.376(8)**
18	**Cl11**	**Mn5**	**2.363(8)**
19	**Cl30**	**Mn5**	**2.380(5)**
20	**Cl32**	**Mn5**	**2.341(6)**
21	**Mn6**	**Cl5**	**2.33(1)**
22	**Mn6**	**Cl13**	**2.36(1)**
23	**Mn6**	**Cl24**	**2.362(7)**
24	**Mn6**	**Cl27**	**2.40(1)**
25	**Cl7**	**Mn7**	**2.37(1)**
26	**Cl9**	**Mn7**	**2.392(9)**
27	**Cl23**	**Mn7**	**2.37(1)**
28	**Cl31**	**Mn7**	**2.31(1)**
29	**Mn8**	**Cl2**	**2.367(9)**
30	**Mn8**	**Cl8**	**2.370(6)**
31	**Mn8**	**Cl16**	**2.376(6)**
32	**Mn8**	**Cl28**	**2.367(7)**

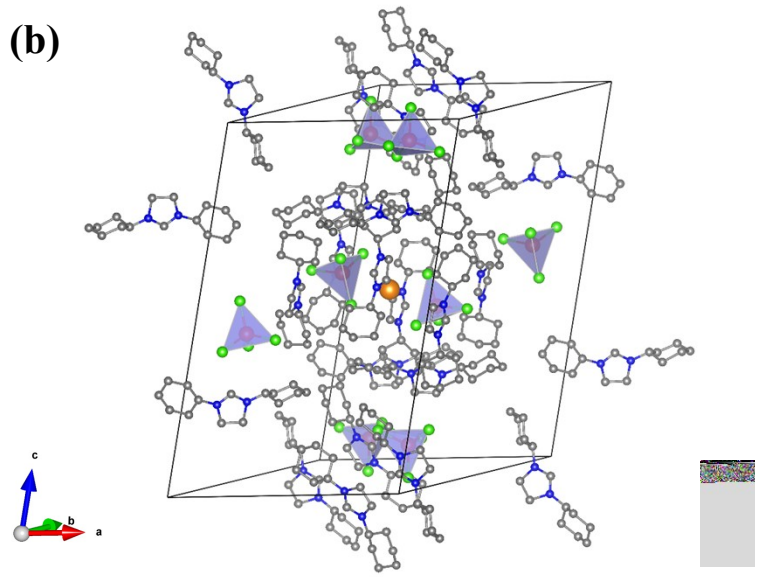
Table S4. Point charge model analysis of **DHIMC**. According to the crystal structure data collected at 278 K (LTP) and 338 K (HTP), respectively. We assume positive charge center influenced by the protonated N, while negative charge center influenced by $MnCl_4^{2-}$ from their equilibrium position within the unit cell.

LTP



Atoms	Atom coordinate		Corrdinate of charge center
Mn	(0.88741,0.16266,0.18478)	(10.88741,0.16266,0.18478)	(0.68229,0.39611,0.48285)
	(0.97220,0.66020,0.67673)	(0.97056,0.61993,0.30141)	
	(0.47728,0.12883,0.28082)	(0.39190,0.63220,0.78913)	
	(0.48150,0.16290,0.64810)	(0.39418,0.67149,0.16466)	
N	(0.1001,0.8637,1.2191)	(0.1082,0.8569,1.136)	(0.49549,0.50525,0.50391)
	(0.5959,0.3708,1.2057)	(0.5958,0.3803,1.1223)	
	(-0.1802,0.1714,1.005)	(-0.0773,0.2198,0.9963)	
	(-0.1802,0.1714,0.005)	(-0.0773,0.2198,-0.0037)	
	(0.9227,1.2198,-0.0037)	(0.8198,1.1714,0.005)	
	(-0.1075,0.4575,0.1777)	(-0.0785,0.3772,0.2499)	
	(0.4727,-0.1632,0.286)	(0.4436,-0.0856,0.2173)	
	(1.1001,-0.1363,0.2191)	(1.1082,-0.1431,0.136)	
	(0.9227,0.2198,-0.0037)	(0.8198,0.1714,0.005)	
	(0.4083,0.7261,-0.0209)	(0.3274,0.6594,-0.0226)	
	(0.1001,0.8637,0.2191)	(0.1082,0.8569,0.136)	
	(0.2611,0.434,0.3276)	(0.2628,0.4129,0.2534)	
	(0.5959,0.3708,0.2057)	(0.5958,0.3803,0.1223)	
	(0.7713,-0.0888,0.3412)	(0.7671,-0.0785,0.2605)	
	(0.9227,0.2198,0.9963)	(0.8198,0.1714,1.005)	
	(1.1297,0.8373,0.743)	(1.0503,0.8187,0.8205)	
	(0.8925,0.4575,0.1777)	(0.9215,0.3772,0.2499)	
	(0.5459,0.1225,0.4598)	(0.4403,0.0745,0.4685)	
	(0.4436,0.9144,0.2173)	(0.4727,0.8368,0.286)	
	(0.1936,1.1327,0.6817)	(0.2522,1.0777,0.7546)	
	(0.0503,0.8187,0.8205)	(0.1297,0.8373,0.743)	
	(0.3274,0.6594,0.9774)	(0.4083,0.7261,0.9791)	
	(0.4403,1.0745,0.4685)	(0.5459,1.1225,0.4598)	
	(-0.0471,0.5656,0.4909)	(0.0538,0.6237,0.4911)	
	(0.1936,0.1327,0.6817)	(0.2522,0.0777,0.7546)	
	(0.3114,0.4708,0.6502)	(0.2422,0.4565,0.7236)	
	(0.7671,0.9215,0.2605)	(0.7713,0.9112,0.3412)	
	(0.8203,-0.0083,0.6412)	(0.7412,-0.0306,0.7125)	
	(1.0538,0.6237,0.4911)	(0.9529,0.5656,0.4909)	
	(0.626,0.3253,0.7533)	(0.5472,0.2982,0.8247)	
	(0.8203,0.9917,0.6412)	(0.7412,0.9694,0.7125)	
	(0.6497,0.6689,0.7076)	(0.721,0.6137,0.776)	

HTP



Atoms	Atom coordinate		Corrdinate of charge center
Mn	(0.21176,0.02587,0.4316)	(0.21001,0.98595,0.05618)	(0.5,0.5,0.5)
	(0.78824,0.97413,0.5684)	(0.29922,0.51611,0.91542)	
	(0.78999,0.01405,0.94382)	(0.29499,0.48313,0.54797)	
	(0.70501,0.51687,0.45203)	(0.70078,0.48389,0.08458)	
N	(1.227,1.0804,0.2448)	(1.1388,1.0175,0.2441)	(0.5,0.5,0.5)
	(0.8612,0.9825,0.7559)	(0.773,0.9196,0.7552)	
	(0.3632,0.6537,1.0918)	(0.4429,0.6769,1.0208)	
	(0.8691,0.1742,1.0844)	(0.9435,0.1899,1.0103)	
	(0.8612,-0.0175,0.7559)	(0.773,-0.0804,0.7552)	
	(-0.1309,0.1742,1.0844)	(-0.0565,0.1899,1.0103)	
	(-0.227,-0.0804,0.7552)	(-0.1388,-0.0175,0.7559)	
	(0.1309,0.8258,0.9156)	(0.0565,0.8101,0.9897)	
	(0.5571,0.3231,0.9792)	(0.6368,0.3463,0.9082)	
	(0.259,0.4276,0.7362)	(0.3631,0.4758,0.7278)	
	(0.29, 0.1901,0.5542)	(0.2614,0.2685,0.4838)	
	(0.1388,0.0175,0.2441)	(0.227,0.0804,0.2448)	
	(0.0565,0.8101,-0.0103)	(0.1309,0.8258,-0.0844)	
	(0.6368,0.3463,-0.0918)	(0.5571,0.3231,-0.0208)	
	(1.1309,0.8258,-0.0844)	(1.0565,0.8101,-0.0103)	
	(0.9435,0.1899,0.0103)	(0.8691,0.1742,0.0844)	
	(0.4429,0.6769,0.0208)	(0.3632,0.6537,0.0918)	
	(0.227,1.0804,0.2448)	(0.1388,1.0175,0.2441)	
	(0.7386,0.7315,0.5162)	(0.71,0.8099,0.4458)	
	(0.4123,0.7346,0.3908)	(0.4148,0.7243,0.4724)	
	(0.6369,0.5242,0.2722)	(0.741,0.5724,0.2638)	

	(0.9241,0.2109,0.4041)	(0.9186,0.2256,0.483)	
	(0.0759,0.7891,0.5959)	(0.0814,0.7744,0.517)	
	(0.5852,0.2757,0.5276)	(0.5877,0.2654,0.6092)	

Figure S3. The PLQY of **DHIMC**.