Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

$[C_6H_{14}N]PbI_3$: One-dimensional perovskite-like order-disorder phase transition material with semiconducting and switchable dielectric attributes

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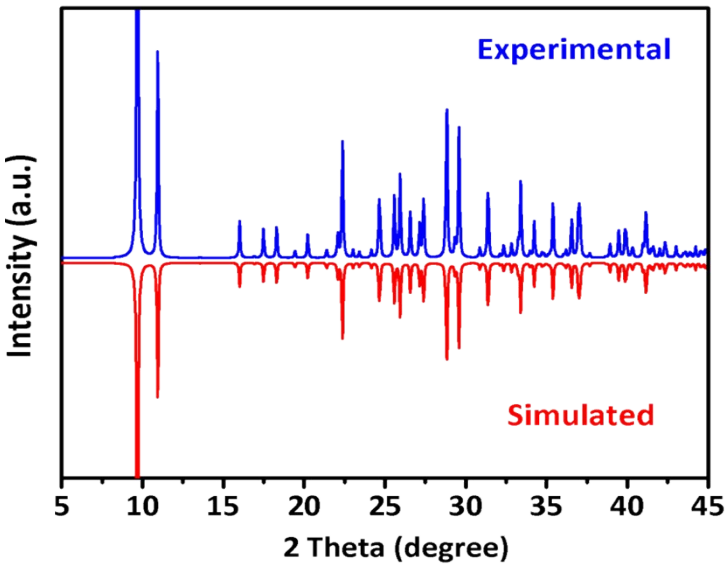

Figure S1. Experimental and simulated PXRD patterns of **MPIP**, verifying the phase purity.

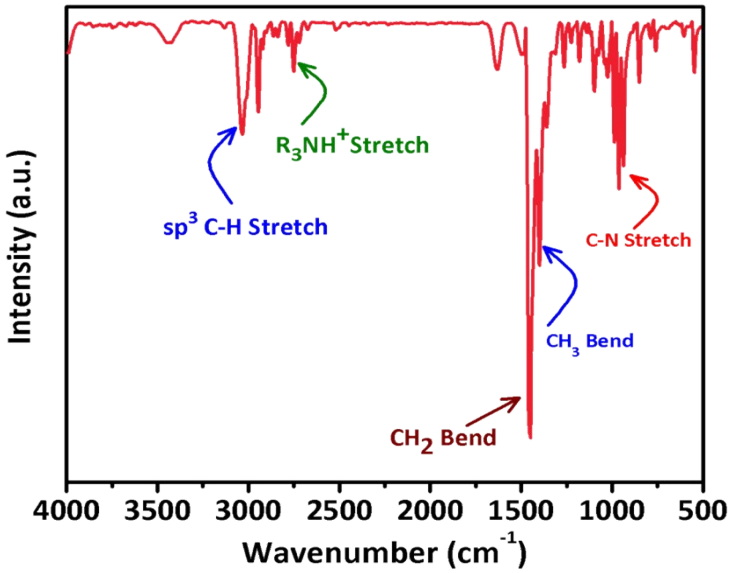

Figure S2. IR Spectrum of **MPIP**.

Table S1. IR spectrum of **MPIP** displays characteristics peaks for stretching and bending vibrations

Group	**Stretching Vibration (cm^{-1})**
sp^3 C-H	3040
C-N	970
Tertiary amine salt (R_3NH^+)	2755
Group	**Bending Vibration (cm^{-1})**
Methyl (CH_3-)	1454
Methylene (-CH_2-)	1394

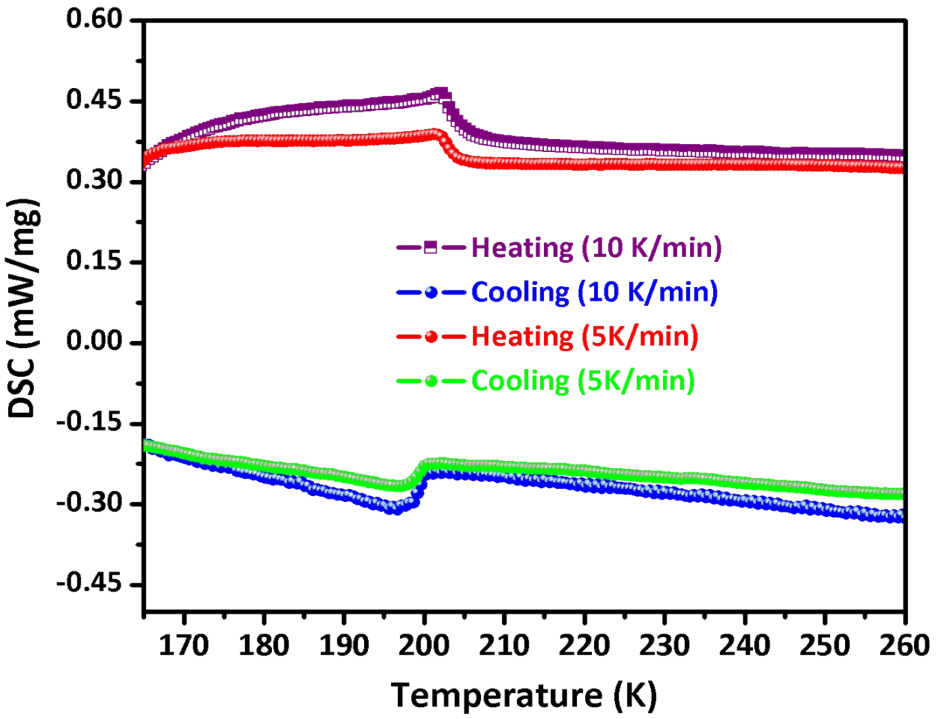

Figure S3. DSC curves performed at different scanning rates (5 K/min and 10 K/min).

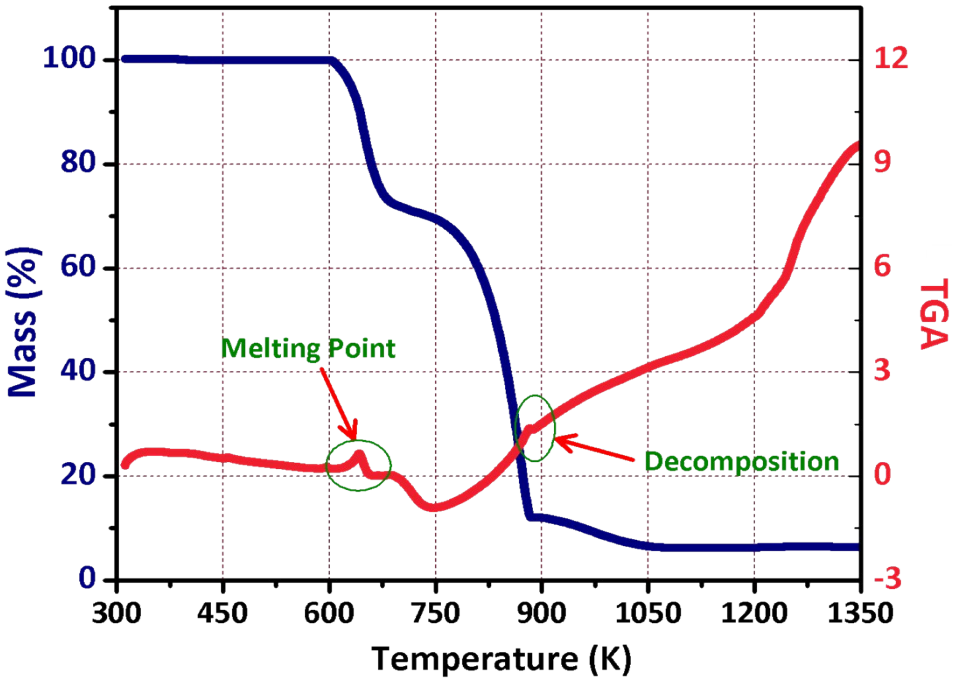

Figure S4. Thermo-Gravimetric Analysis (TGA) spectrum of **MPIP**, shows its high thermal stability.

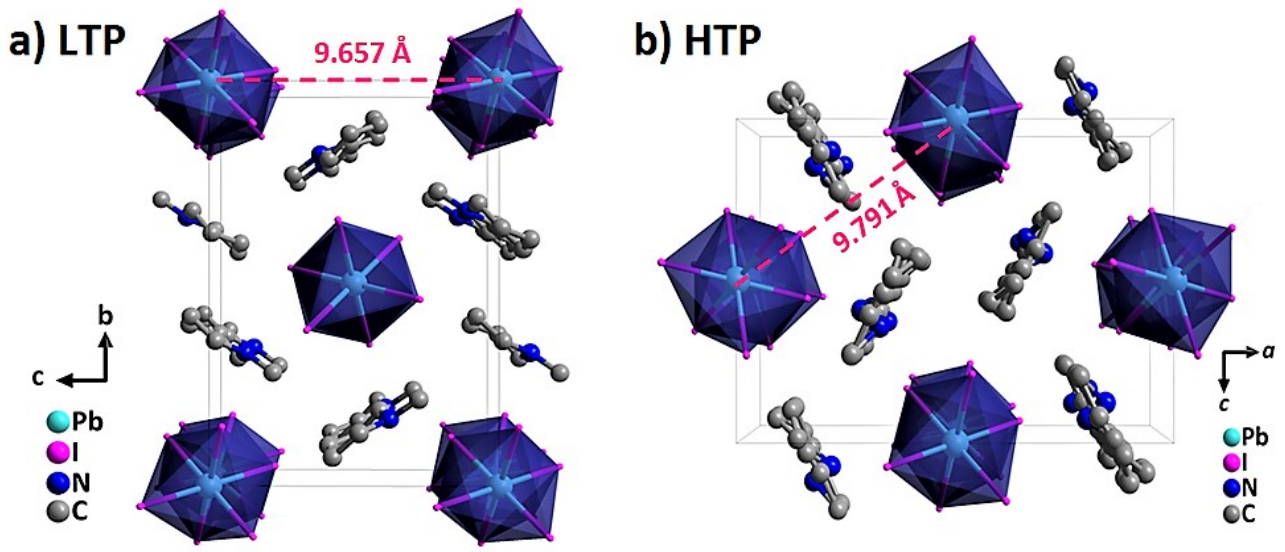

Figure S5. Packing diagram of **MPIP** a) at 180 K (LTP) in the *c*-direction and b) at 280 K (HTP) in the *b*-direction. The distance between the Pb-atoms in adjacent planes is 9.657 Å at LTP, and is 9.791 Å at HTP.

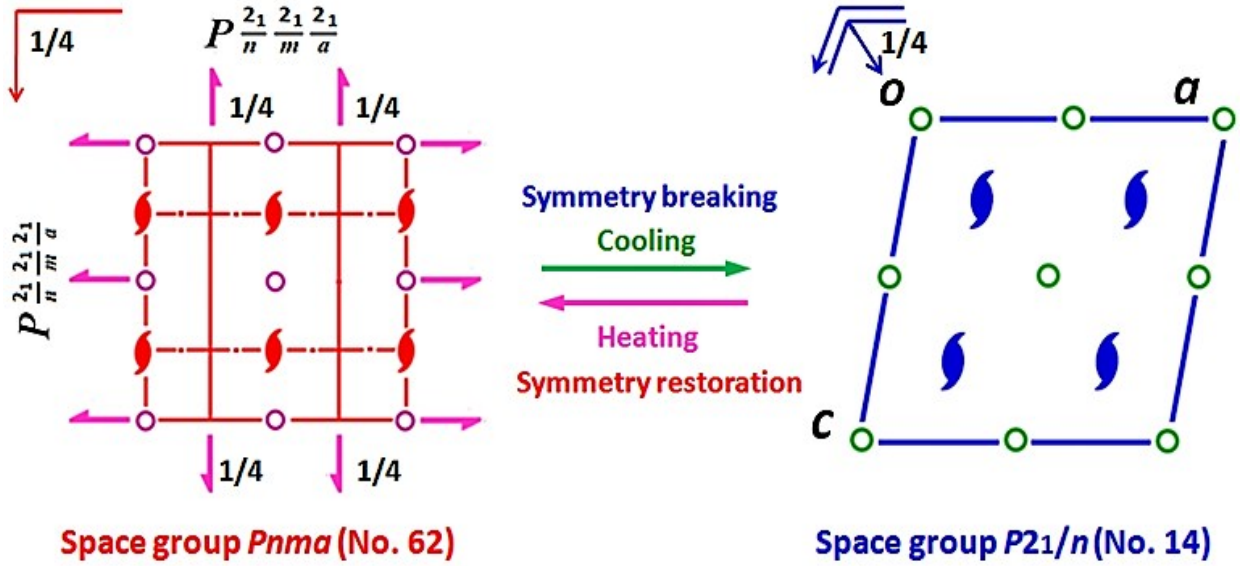

Figure S6. Symmetry breaking process in **MPIP** occurring from *Pnma* (HTP) to $P2_1/n$ (LTP). [S1]

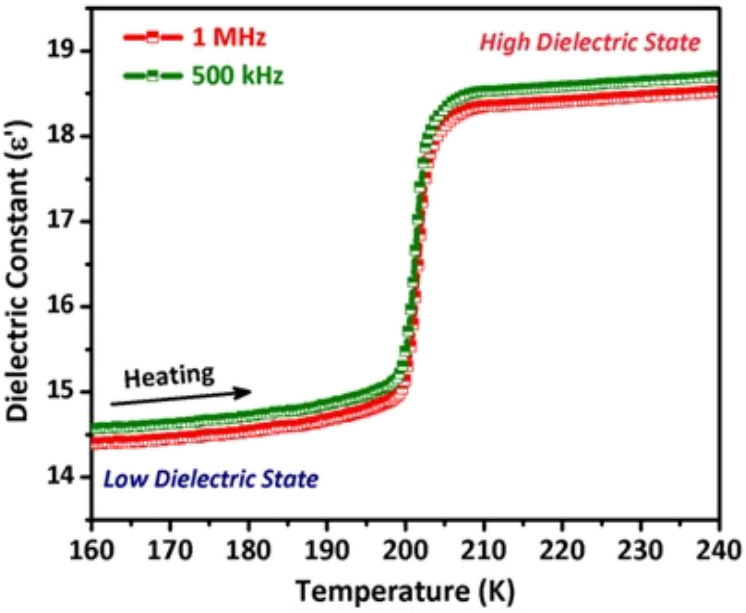

Figure S7. Temperature-dependent dielectric constant measured on heating mode at 500 kHz and 1 MHz for **MPIP**

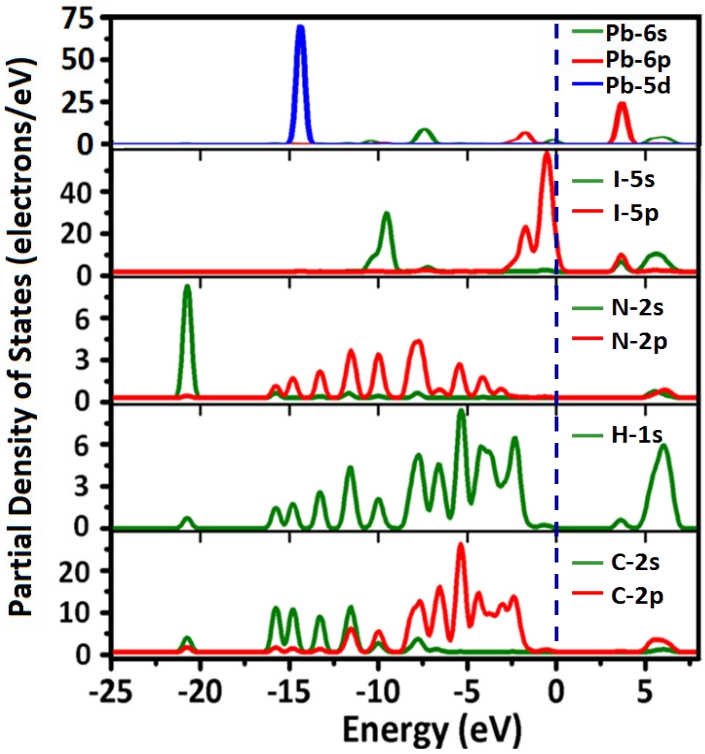

Figure S8. Partial density of states (PDOS) of **MPIP**

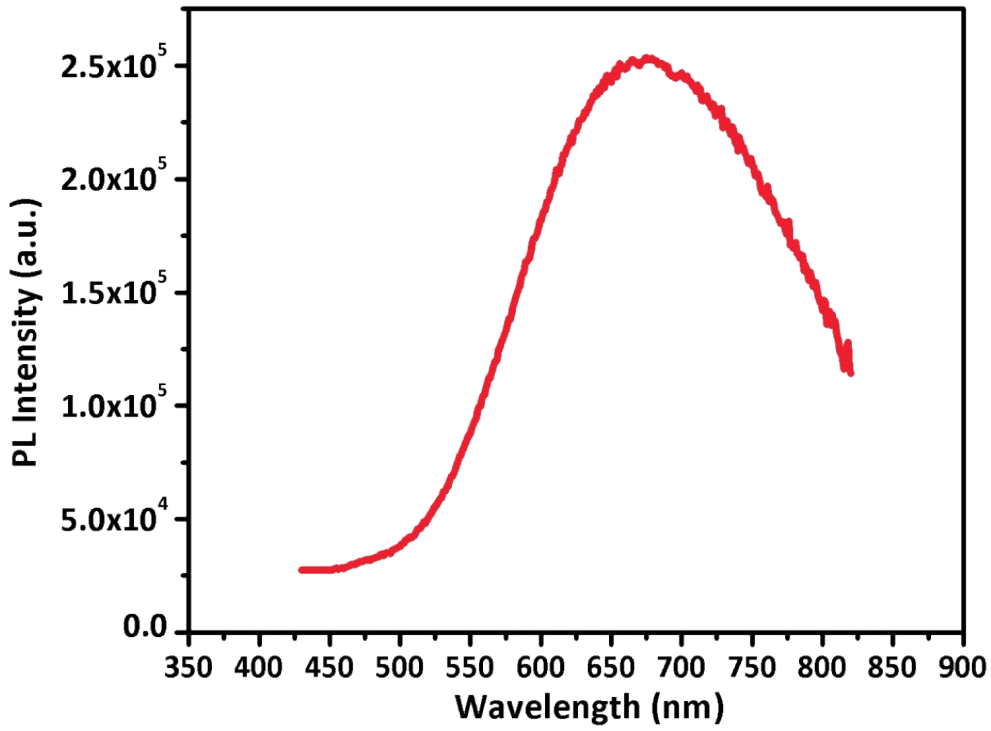

Figure S9. Emission spectrum (λ_{ex} = 365 nm) of **MPIP** performed at room temperature

Table S2. The SCXRD data and structure refinement details of **MPIP** at 280 K and 180 K.

Temperature (*K*)	280 K, Mo-*K*α	180 K, Mo-*K*α
Sum formula	$C_6H_{14}PbI_3N_1$	$C_6H_{14}PbI_3N_1$
Moiety formula	$C_6H_{14}N$, PbI_3	$C_6H_{14}N$, PbI_3
Formula Weight	1375.84	688.07
Crystal system	Orthorhombic	Monoclinic
	Pnma	$P\,2_1/n$
Cell parameters	*a*= 16.1575 (11) Å *b*= 8.0428 (5) Å *c*= 11.0622 (9) Å α= 90° β= 90° γ= 90°	*a*= 8.0436 (8) Å *b*= 15.8720 (16) Å *c*= 11.0048 (13) Å α= 90° β= 92.088(9)° γ= 90°
Volume (Å^3)	1437.55(18)	1404.0(2)
Z	2	4
*ρ*cal. (g/cm^3)	3.179	3.255
F(000)	1192.0	1192.0
Theta range (°)	3.9110-28.3620	3.6260 - 28.7340
Limiting indices	-19<=*h*<=16, -9<=*k*<=9, -8<=*l*<=13	-9<=*h*<=9, -18<=*k*<=18, -13<=*l*<=13
Completeness	99.8%	99.60%
GOF on F^2	1.069	1.239
Reflections collected / unique	4217/1363 (R_{int} = 0.0777)	7598/2462 (R_{int} = 0.0751)
Final R indexes [on $F_\circ^2$ $I > 2\sigma(I)$]	R_1 = 0.0496, wR_2 = 0.1181	R_1 = 0.1065, wR_2 = 0.2949
Final R indexes [all data]	R_1 = 0.0607, wR_2 = 0.1285	R_1 = 0.1197, wR_2 = 0.3182

$$\alpha R_1 = \Sigma\,[(F_o) - (F_c)]\,/\,\Sigma\,[F_o],\ wR_2 = [\Sigma\,(|F_o|^2 - |F_c|^2)\,/\,\Sigma|F_o|^2]^{1/2}$$

Table S3. Selected Bond Angles [°] for **MPIP** at 280 K and 180 K

Temperature	Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
280 K	Pb1[1]	I1	Pb1	76.89(2)	I2[3]	Pb1	I1[3]	86.46(3)
	Pb1	I2	Pb1[1]	77.08(2)	I2	Pb1	I1	86.46(3)
	Pb1[2]	I3	Pb1	76.94(3)	I2[3]	Pb1	I1	93.54(3)
	I1[3]	Pb1	I1	180.0	I2	Pb1	I1[3]	93.54(3)
	I2	Pb1	I2[3]	180.0	I2	Pb1	I3	95.74(3)
	I3[3]	Pb1	I3	180.0	I2[3]	Pb1	I3	84.26(3)
					I2	Pb1	I3[3]	84.26(3)
					I3[3]	Pb1	I1[3]	94.67(3)
					I3	Pb1	I1[3]	85.33(3)
					I3[3]	Pb1	I1	85.33(3)
					I3	Pb1	I1	94.67(3)
	Symmetry Codes: [1]1/2+X,+Y,3/2-Z; [2]1/2+X,-1+Y,3/2-Z; [3]3/2+X,3/2-Y,5/2-Z; [4]+X,3/2-Y,+Z							
Temperature	**Atom**	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
180 K	I3	Pb1	I4[3]	83.95(4)	I3	Pb2	I4	95.80(4)
	I3[2]	Pb1	I4[3]	96.05(4)	I3[3]	Pb2	I4	84.20(4)
	I3[2]	Pb1	I4[4]	83.95(4)	I3	Pb2	I4[3]	84.20(4)
	I3	Pb1	I4[4]	96.05(4)	I3[3]	Pb2	I4[3]	95.80(4)
	I5[4]	Pb1	I3	93.84(4)	I3	Pb2	I5[3]	86.06(4)
	I5[4]	Pb1	I3[2]	86.16(4)	I3	Pb2	I5	93.94(4)
	I5[3]	Pb1	I3	86.16(4)	I3[3]	Pb2	I5	86.06(4)
	I5[3]	Pb1	I3[2]	93.84(4)	I3[3]	Pb2	I5[3]	93.94(4)
	I5[3]	Pb1	I4[4]	94.74(4)	I4	Pb2	I5	85.28(4)
	I5[3]	Pb1	I4[3]	85.26(4)	I4[3]	Pb2	I5	94.72(4)
	I5[4]	Pb1	I4[3]	94.74(4)	I4[3]	Pb2	I5[3]	85.28(4)
	I5[4]	Pb1	I4[4]	85.26(4)	I4	Pb2	I5[3]	94.72(4)
	I3[2]	Pb1	I3	180.0	I3[3]	Pb2	I3	180.0
	I4[4]	Pb1	I4[3]	180.0	I4	Pb2	I4[3]	180.0
	I5[4]	Pb1	I5[3]	180.0	I5[3]	Pb2	I5	180.0
					Pb1[1]	I5	Pb2	77.29(3)
					Pb2	I3	Pb1	77.41(3)
					Pb2	I4	Pb1[1]	77.03(3)
	Symmetry Codes: [1]1-X,-Y,-Z; [2]3/2-X,3/2+Y,3/2-Z; [3]5/2-X,3/2+Y,3/2-Z; [4]-1-X,-Y,-Z							

Table S4. Selected Bond Lengths [Å] for **MPIP** at 280 K and 180 K

Temperature	Atom	Atom	Bond Length (Å)	Atom	Atom	Length (Å)
280 K	Pb1	I1[1]	3.2339(9)	I1	Pb1[2]	3.2338(9)
	Pb1	I1	3.2339(9)	I2	Pb1[2]	3.2270(8)
	Pb1	I2	3.2269(9)	I3	Pb1[3]	3.2321(9)
	Pb1	I2[1]	3.2270(8)	Pb1	Pb1	4.022
	Pb1	I3[1]	3.2321(9)			
	Pb1	I3	3.2322(9)			
	Symmetry Codes: [1]3/2+X,3/2-Y,5/2-Z; [2]1/2+X,+Y,3/2-Z; [3]1/2+X,-1+Y,3/2-Z; [4]+X,3/2-Y,+Z					
Temperature	**Atom**	**Atom**	**Bond Length (Å)**	**Atom**	**Atom**	**Length (Å)**
180 K	Pb1	I3	3.2181(14)	Pb2	I3	3.2137(14)
	Pb1	I3[1]	3.2181(14)	Pb2	I3[3]	3.2137(14)
	Pb1	I4[2]	3.2348(16)	Pb2	I4	3.2237(15)
	Pb1	I4[3]	3.2348(16)	Pb2	I4[3]	3.2237(15)
	Pb1	I5[2]	3.2148(16)	Pb2	I5[3]	3.2252(16)
	Pb1	I5[3]	3.2148(16)	Pb2	I5	3.2252(16)
				I4	Pb1[4]	3.2348(16)
				I5	Pb1[4]	3.2148(16)
				Pb1	Pb1	4.022
	Symmetry Codes: [1]3/2-X,3/2+Y,3/2-Z; [2]-1-X,-Y,-Z; [3]5/2-X,3/2+Y,3/2-Z; [4]1-X,-Y,-Z					

Table S5. Hydrogen-Bond Geometry (Å, degree) for the N–H···I at 280 K and 180 K in **MPIP**

	D–H···A	H···A [Å]	D···A [Å]	D–H···A [°]
280 K	N1–H1A···I1	3.097	3.97	164.41
	N1A–H1AA···I3	2.768	3.66	173.37
180 K	N7–H7···I4	2.895	3.816	171.14

Calculation of 'ΔS' and '*N*' For MPIP:

According to Boltzmann equation:

$$\Delta S = nR\ln N$$

Where;

ΔS = entropy change, extracted from the C_P data,

R = the universal gas constant,

n = the number of guest particles per mole (n =1, here), and

N = the number of possible orientations for the disordered system.

The ΔS and N values on the heating process of **MPIP** are calculated as follows: [S2]

$$\Delta S = \int_{T_1}^{T_2} \frac{Q}{T}_{dT}$$

$$\Delta S \cong \frac{\Delta H}{T_c}$$

$$\Delta S = \frac{1.795\ J\ g^{-1} \times\ 688.07\ g\ mol^{-1}}{201\ K}$$; where 688.07 g mol^{-1} is a formula weight of **MPIP**.

$$\Delta S = \frac{1235.08\ J\ mol^{-1}}{201\ K}$$

$$\Delta \mathbf{S = 6.145\ J}\ mol^{-1}K^{-1}$$

$$\Delta S = R\ln N$$

$$N = e^{(\frac{\Delta S}{R})}$$

$$N = e^{\left(\frac{6.145\ J\ mol^{-1}K^{-1}}{8.314\ J\ mol^{-1}K^{-1}}\right)}$$

***N* = 2.09**

References:

1. T. Hahn, *International Tables for Crystallography*, *Vol. A: Space-Group Symmetry*, 5th edn., Springer, **2005**.
2. Y.-Z. Tang, Z.-F. Gu, J.-B. Xiong, J.-X. Gao, Y. Liu, B. Wang, Y.-H. Tan and Q. Xu, *Chem. Mater*., 2016, **28**, 4476−4482.