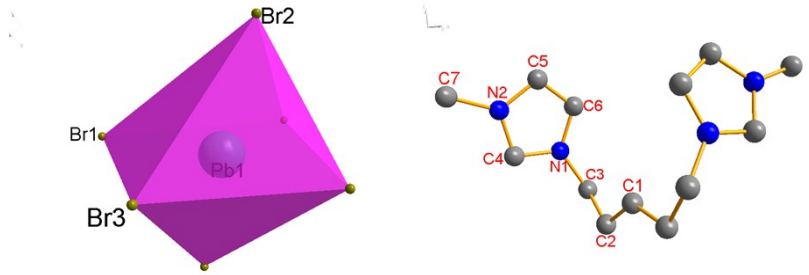
ESI

Table S1: Selected bond lengths and bond angles of **1** at 298, 373 and 413 K.



Bond lengths(Å)			
Temperature / K	298	373	413
N(1)-C(4)	1.317(17)	1.30(3)	1.29(2)
N(1)-C(3)	1.46(2)	1.49(4)	1.45(3)
N(2)-C(4)	1.342(17)	1.35(3)	1.32(3)
C(1)-C(2A)	1.30(5)	1.26(7)	1.22(8)
C(2)-C(3)	1.57(4)	1.48(7)	1.53(8)
N(1)-C(6)	1.38(2)	1.37(3)	1.39(5)
Br(2)-Pb(1C)	3.128(2)	3.131(5)	3.140(6)
Pb(1)-Br(1)	3.194(3)	3.211(4)	3.208(6)
Pb(1)-Br(3B)	3.005(3)	3.001(5)	3.007(6)
Pb(1)-Br(1C)	3.194(3)	3.211(4)	3.208(6)
N(2)-C(5)	1.360(19)	1.37(4)	1.36(4)
N(2)-C(7)	1.453(18)	1.45(4)	1.45(4)
C(1)-C(2)	1.33(4)	1.26(7)	1.22(8)
C(5)-C(6)	1.292(2)	1.32(5)	1.28(4)
Pb(1)-Br(2)	3.128(3)	2.950(4)	3.140(5)
Pb(1)-Br(3)	3.016(3)	3.045(5)	3.046(6)
Pb(1)-Br(2B)	3.128(3)	3.131(5)	3.140(5)
Br(1)-Pb(1B)	3.190(2)	3.211(4)	3.208(4)
Br(3)-Pb(1C)	3.005(3)	3.001(4)	3.007(6)
Bond angles(°)			
Temperature / K	298	373	413
C(4)-N(1)-C(6)	106.6(13)	106(3)	104(3)
C(6)-N(1)-C(3)	128.2(14)	128(3)	129(3)
C(5)-N(2)-C(7)	127.0(12)	128(2)	126(3)
C(2A)-C(1)-C(2)	142(7)	147(10)	148(10)

N(1)-C(3)-C(2)	114.2(16)	113(3)	114(3)
N(1)-C(4)-N(2)	108.7(13)	112(3)	114(3)
C(5)-C(6)-N(1)	109.4(15)	109(3)	108(3)
Br(2)-Pb(1)-Br(3)	85.93(9)	85.38(15)	85.4(2)
Br(2)-Pb(1)-Br(3B)	93.93(4)	94.24(9)	94.49(9)
Br(3)-Pb(1)-Br(3B)	179.66(5)	179.52(19)	179.7(2)
Br(1)-Pb(1)-Br(2B)	82.75(8)	83.23(14)	83.09(19)
Br(3B)-Pb(1)-Br(2B)	82.79(9)	82.02(14)	82.69(19)
Br(1)-Pb(1)-Br(1C)	173.40(10)	173.17(17)	173.6(2)
Br(3B)-Pb(1)-Br(1C)	98.82(4)	98.78(8)	98.81(6)
C(4)-N(1)-C(3)	125.2(15)	126(3)	127(3)
C(4)-N(2)-C(7)	125.2(12)	127(2)	130(3)
C(1)-C(2)-C(3)	118(4)	131(8)	130(9)
C(5)-C(6)-N(1)	109.4(15)	109(3)	108(3)
C(6)-C(5)-N(2)	107.5(17)	108(3)	110(4)
Br(2)-Pb(1)-Br(1)	102.11(4)	101.66(7)	101.44(7)
Br(1)-Pb(1)-Br(3)	93.82(4)	93.81(6)	94.06(6)
Br(1)-Pb(1)-Br(3B)	86.15(9)	86.49(14)	86.2(2)
Br(2)-Pb(1)-Br(2B)	175.38(11)	176.12(18)	176.0(2)
Br(3)-Pb(1)-Br(2B)	97.33(4)	97.38(8)	97.46(9)
Br(2)-Pb(1)-Br(1C)	81.56(8)	81.44(13)	81.69(18)
Br(3)-Pb(1)-Br(1C)	81.47(8)	80.88(14)	80.88(19)
Br(2B)-Pb(1)-Br(1C)	102.11(3)	101.66(7)	101.44(7)

Table S2: Crystallographic data and refinement parameters of **1** at 298 K using order and disorder model for C2.

Model	disorder	order
Wavelength (Å)	0.71073	0.71073
Empirical formula	$C_{13}H_{22}Br_6N_4Pb_2$	$C_{13}H_{22}Br_6N_4Pb_2$
Formula weight	1128.14	1128.14
Crystal system	Orthorhombic	Orthorhombic
Space group	*Fdd2*	*Fdd2*
a (Å)	29.498(4)	29.498(4)
b (Å)	22.319(3)	22.319(3)
c (Å)	7.7732(9)	7.7732(9)
α (°)	90.00	90.00
β (°)	90.00	90.00
γ (°)	90.00	90.00
V (Å^3)/Z	5117.6(11)/8	5117.6(11)/8
ρ (g·cm^{-1})	2.929	2.913
F(000)	3968	3968
Abs. coeff. (mm^{-1})	22.516	22.516
θ Ranges (data collection; °)	2.289 - 25.494	2.29 - 27.56
Index ranges	-35 ≤ h ≤ 35	-37 ≤ h ≤ 38
	-26 ≤ k ≤ 26	-28 ≤ k ≤ 27
	-9 ≤ l ≤ 8	-10 ≤ l ≤ 8
R_{int}	0.00599	0.0625
Independent reflections/restraints/parameters	2275/1/126	2762/1/108
Goodness of fit on F^2	1.007	1.024
R_1, wR_2[a] [$I>2\sigma$(I)]	0.0346, 0.0728	0.0418, 0.0961
R_1, wR_2[a] [all data]	0.0568, 0.0778	0.0795, 0.1102
Residual (e·nm^{-3})	1.000/-1.750	1.362/-2.093

Table S3: CIE chromaticity of **1** at different temperatures

Temperature	CIE x	CIE y	Peak center location(nm) (compound light)	Relative intensity
10K	0.1936	0.0792	449	10280900
25K	0.2802	0.1404	450	3671650
40K	0.3931	0.2099	680	2662720
55K	0.4854	0.2756	676	2532070
70K	0.5544	0.3264	673	2589850
85K	0.579	0.3558	669	2414010
100K	0.5882	0.3748	668	2209770
125K	0.5846	0.3948	632	1566020
150K	0.5719	0.4115	686	857094
175K	0.5594	0.4242	626	612023
200K	0.54	0.4392	613	310040
225K	0.5284	0.4441	618	147573
250K	0.5085	0.4491	613	57889
275K	0.497	0.4455	593	32960
300K	0.4716	0.4403	613	13482

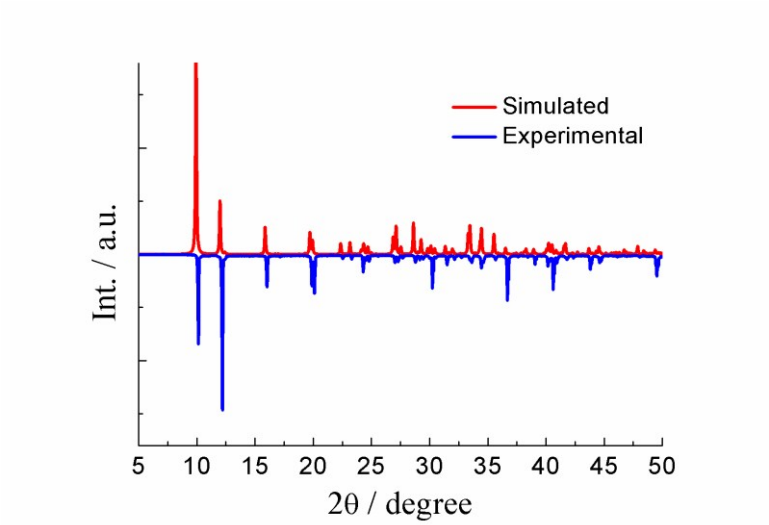
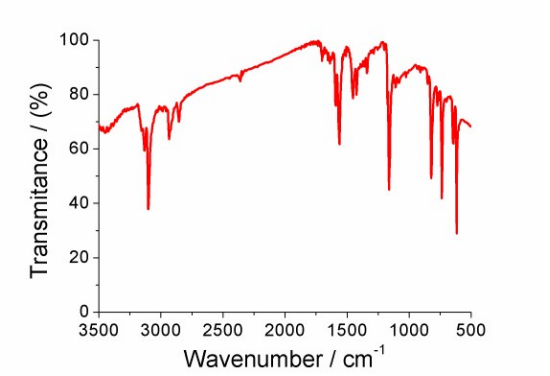


Fig. S1: Powder X-ray diffraction patterns for as-prepared sample of **1**, confirming the phase purity of the as-prepared sample (Black lines: experimental patterns; red lines: simulated profiles).



Vibration bands	Assignment
3103s ,2929s ,2854s	ν_{C-H}
1563s	$\nu_{-C=N}$
1455s ,1421s	$\delta_{as\ C-H}$ ($-CH_3$)
1167s	δ_{C-H} (inside of plane)
821s ,737s ,617s	$\delta_{=C-H}$ (out of plane)

Fig. S2: FT-IR spectra and bands assignment for **1**.

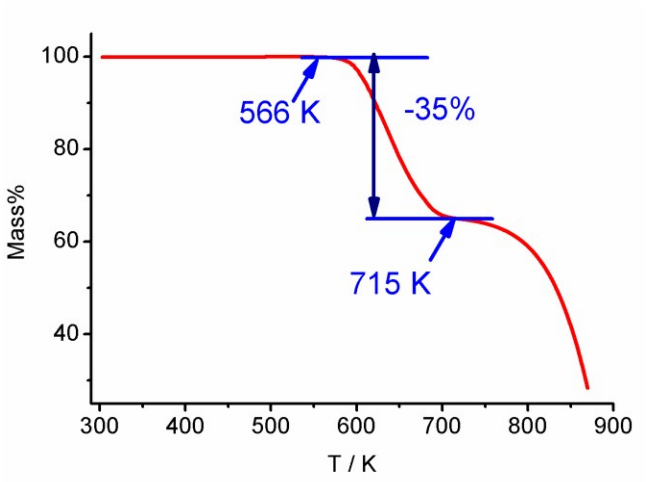


Fig. S3: TG plot of **1** between 303 K and 873 K.

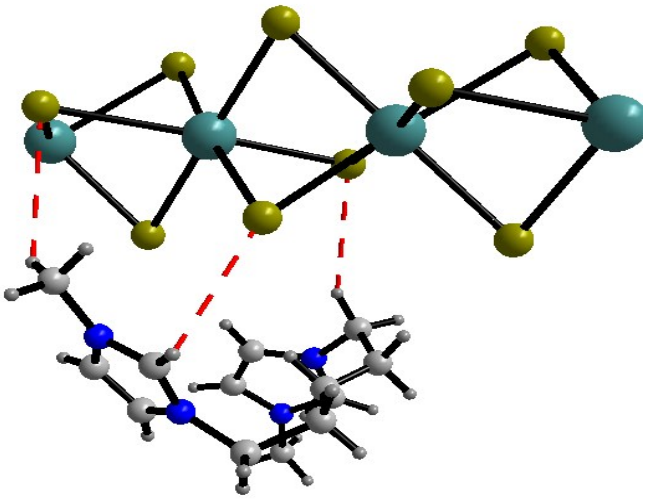


Fig. S4: The charge-assisted H-bonding interactions between the CH_2 groups of the cations and the Br^- ions of the inorganic chains.

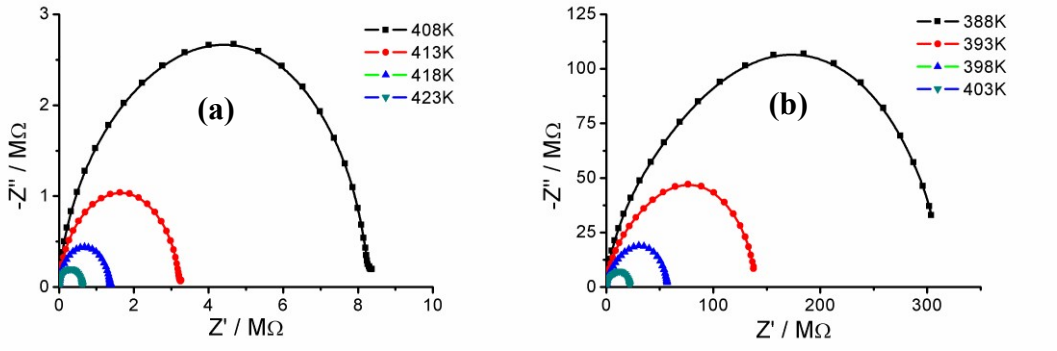


Fig. S5: (a) and (b) Nyquist plots of **1** at selected temperature.

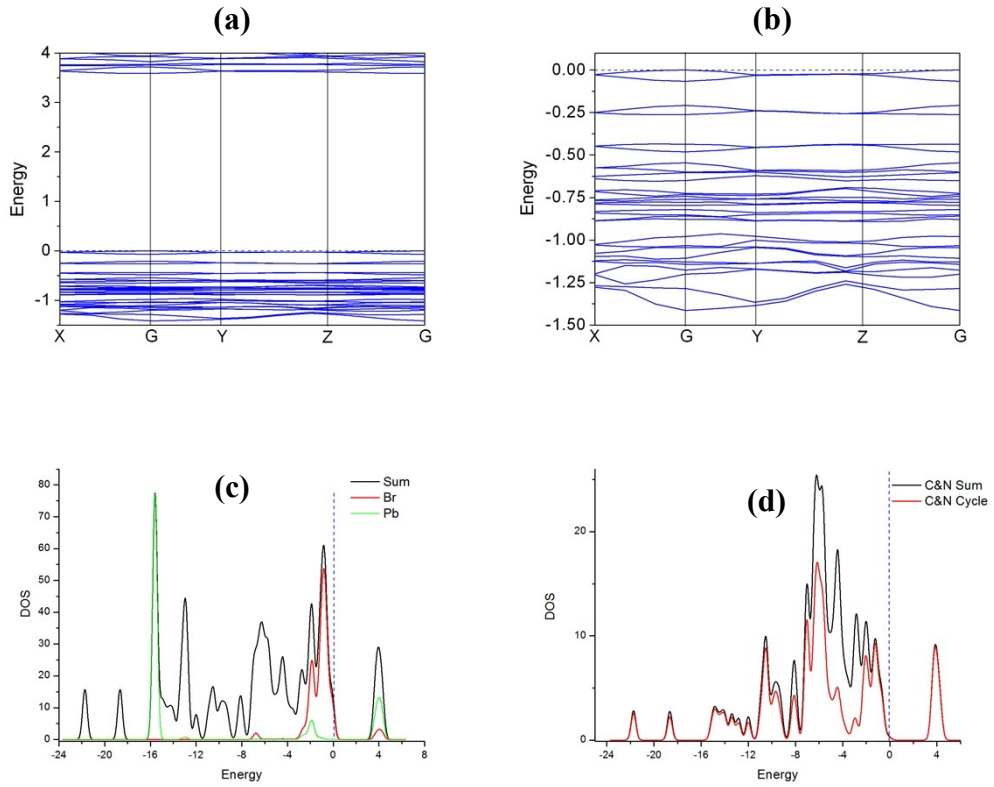


Fig. S6 (a) Several highest occupied band and the lowest unoccupied bands calculated using crystal structure at 298 K with band gap of 3.57 eV (b) enlarged one (c) DOC of whole anion and cation and PDOS of Pb^{2+} and Br^- (d) PDOS of cation and imidazole ring.

Calculation for electronic band structure and densities of states (DOS) was performed using the CASTEP program[1] on the non-modelized crystal structure of **1** which was obtained from X-ray single crystal structure analyses at 298 K. The generalized

gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)[2] is used for the exchange-correlation functional. The k-points in the Brilliouin zone were set to be 3×3×4 according to the Monkhorst-Pack scheme.[3]

The calculation indicated that the energy levels near to the Fermi level include contributions of both cations and anionic chains, demonstrating that the light absorption below 400 nm in UV-vis spectrum of **1** in solid state arises from both the electron transition of $\pi^* \leftarrow \pi$ within the imidazole rings and from valence band to conducting band within the one-dimensional inorganic $PbBr_3^-$ chains.

References

1. (a) M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne, *J. Phys.: Condens. Matter,* 2002, **14**, 2717; (b) V. Milman, B. Winkler, J. A. White, C. J. Pickard, M. C. Payne, E. V. Akhmatskaya and R. H. Nobes, *Int. J. Quantum Chem.,* 2000, **77**, 895.
2. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.,* 1996, **77**, 3865.
3. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B,* 1976, **13**, 5188.

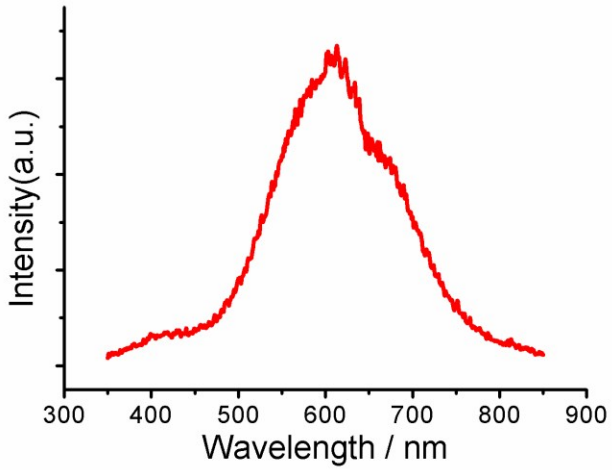


Fig. S7 PL spectrum for **1** at 300 K with λ_{ex} = 323 nm.

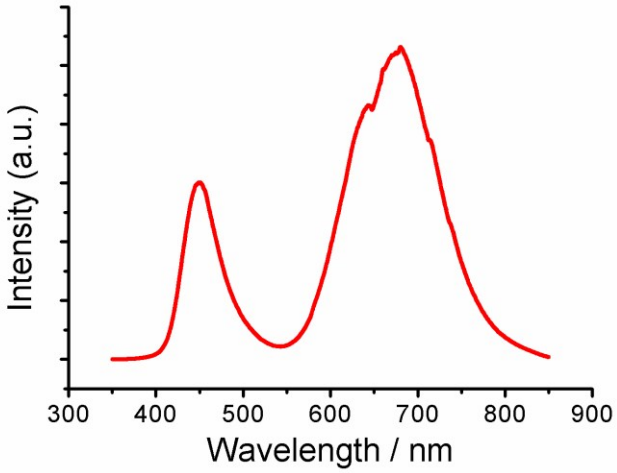


Fig. S8: PL spectra for **1** at 40 K with λ_{ex} = 323 nm.

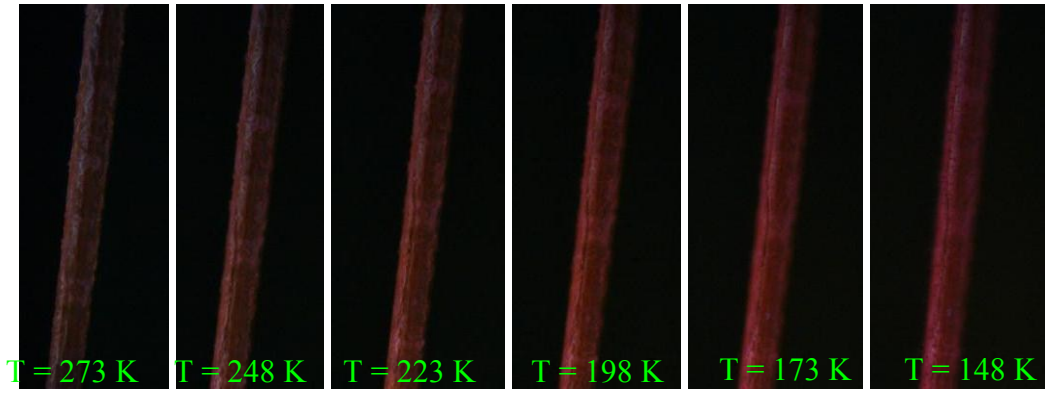


Fig. S9: Hot stage microscope pictures of **1** under excitation with λ_{ex} = 330 nm at selected temperatures.