Electronic Supplementary Information

Synthesis, characterization, and theoretical analysis of $(NH_4)_3PbCl_5$

Liang Zhu,[a,b] Wenqi Jin,[a,b] ZhihuaYang,[a,b] Yun Yang,[a,b*] Shilie Pan[a,b*]

[a]CAS Key Laboratory of Functional Materials and Devices for Special Environments; Xinjiang Technical Institute of Physics & Chemistry, CAS; Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40-1 South Beijing Road, Urumqi 830011, China.

[b]Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.

*Corresponding author: slpan@ms.xjb.ac.cn.

Table S1. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of $(NH_4)_3PbCl_5$. U(eq) is defined as one third of the trace of the orthogonalizedU_{ij} tensor.

Atoms	x	y	z	$U_{(eq)}$
Pb(1)	5804.8(3)	7500	6531.7(3)	26.32(14)
N(1)	4224(7)	7500	1479(6)	16.9(12)
N(2)	2564(6)	5467(3)	4645(6)	39.5(12)
Cl(1)	2789(2)	7500	5217(2)	26.9(4)
Cl(2)	6138.9(18)	8782.4(9)	3719.9(16)	31.2(3)
Cl(3)	4431(2)	8793.9(11)	8244.1(17)	40.5(4)
H(1A)	4395	7500	448	20
H(1B)	3208	7500	1667	20
H(1C)	4642	7959	1903	20
H(2A)	2553	5361	3613	47
H(2B)	3401	5216	5083	47
H(2C)	1680	5267	5083	47
H(2D)	2626	6022	4801	47

Table S2. Selected bond lengths (Å) and angles (deg.) for $(NH_4)_3PbCl_5$.

Pb(1)-Cl(1)#1	3.2220(27)	N(1)-H(1A)	0.885
Pb(1)-Cl(2)	3.1396(23)	N(1)-H(1B)	0.872
Pb(1)-Cl(2)#2	3.1396(23)	N(1)-H(1C)	0.883
Pb(1)-Cl(3)	2.7619(22)	N(1)-H(1C)#4	0.883
Pb(1)-Cl(3)#3	2.7619(22)	N(2)-H(2A)	0.890
Pb(1)-Cl(1)	2.7768(26)	N(2)-H(2B)	0.891
H(1A)-N(1)-H(1C)	109.6	N(2)-H(2C)	0.891
H(1B)-N(1)-H(1C)	108.6	N(2)-H(2D)	0.889
H(1A)-N(1)-H(1B)	110	H(2A)-N(2)-H(2B)	109.5
H(1A)-N(1)-H(1C)#4	109.6	H(2A)-N(2)-H(2C)	109.5
H(1B)-N(1)-H(1C)#4	108.6	H(2B)-N(2)-H(2C)	109.4
H(1C)-N(1)-H(1C)#4	110.5	H(2A)-N(2)-H(2D)	109.4
H(2C)-N(2)-H(2D)	109.7	H(2B)-N(2)-H(2D)	109.3

Symmetry transformations used to generate equivalent atoms:

#1 0.5+x,1.5-y,1.5-z #2x,1.5-y,z #3 x, 1.5-y,z #4x,1.5-y,z

Table S3. Hydrogen bond lengths (Å) and angles (º) for $(NH_4)_3PbCl_5$. D, hydrogen bond donor; A, hydrogen bond acceptor.

D-H···A	$\mathbf{d_{(D-H)}}$	$\mathbf{d_{(H\cdots A)}}$	$\mathbf{d_{(D\cdots A)}}$	＜（DHA）
N(1)-H(1A) ···Cl(3)	0.885	2.769	3.4230	131.820
N(1)-H(1B) ···Cl(2)	0.872	2.695	3.3028	127.919
N(1)-H(1C) ···Cl(2)	0.883	2.378	3.2122	157.640
N(2)-H(2A) ···Cl(2)	0.890	2.676	3.3123	129.381
N(2)-H(2B) ···Cl(2)	0.891	2.513	3.1944	133.798
N(2)-H(2C) ···Cl(3)	0.891	2.794	3.3976	126.216
N(2)-H(2D) ···Cl(1)	0.889	2.367	3.2552	179.955

Figure S1. Asymmetric unit of $(NH_4)_3PbCl_5$.

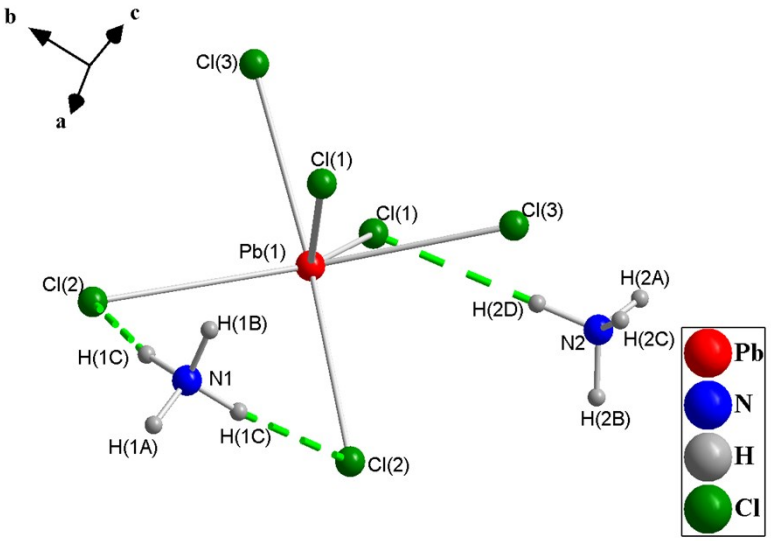

Figure S2. The hydrogen bonds and their connect environments in $(NH_4)_3PbCl_5$.

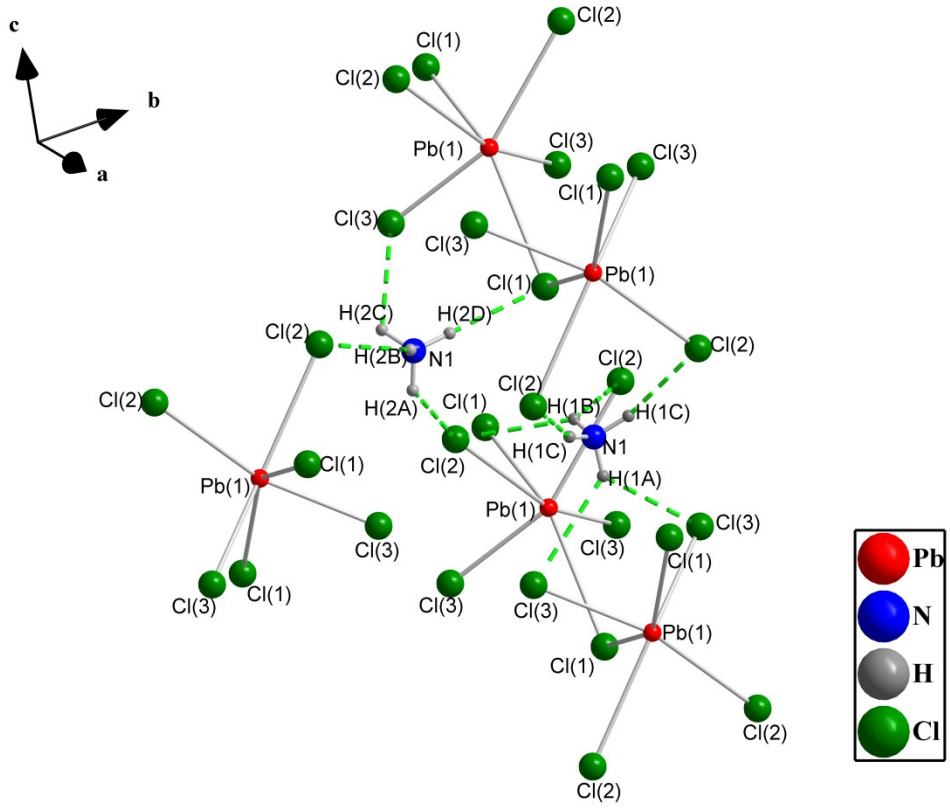

Figure S3. The $[N_2H_8Cl_9]^{7-}$ dimmer (a) and $[Rb_2Cl_{14}]^{12-}$ dimmer (b).

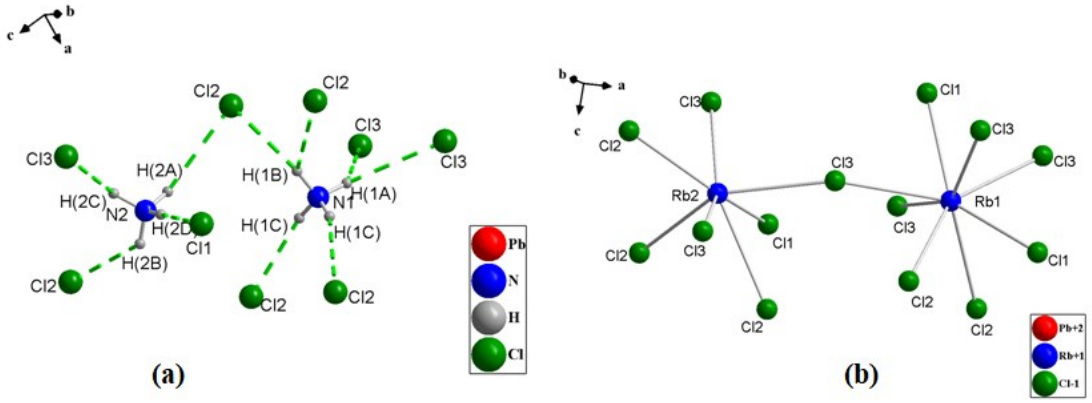

Figure S4. IR spectroscopy of $(NH_4)_3PbCl_5$.

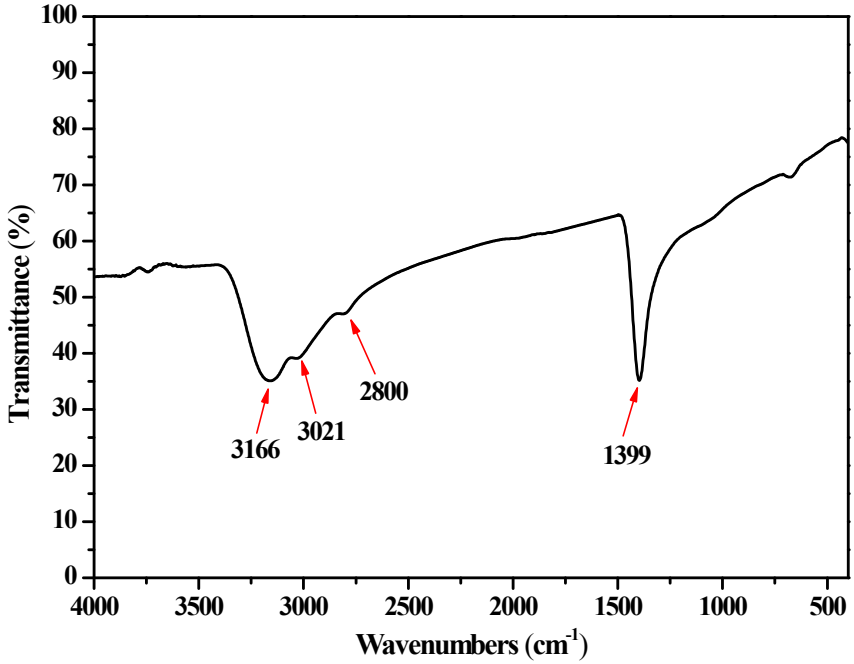

Figure S5. UV-Vis-NIR diffuse reflectance spectrum of $(NH_4)_3PbCl_5$.

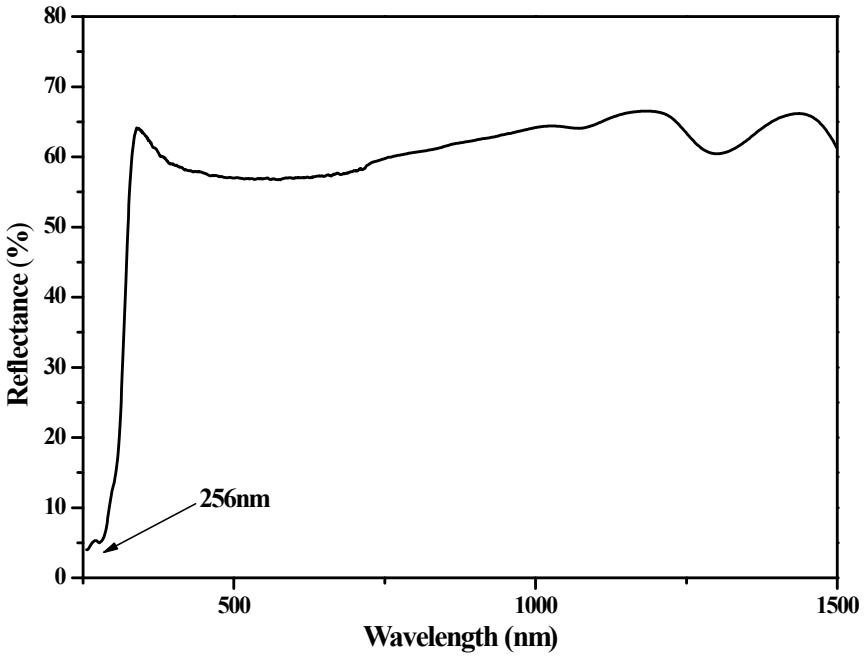

Figure S6. Thermal stability.

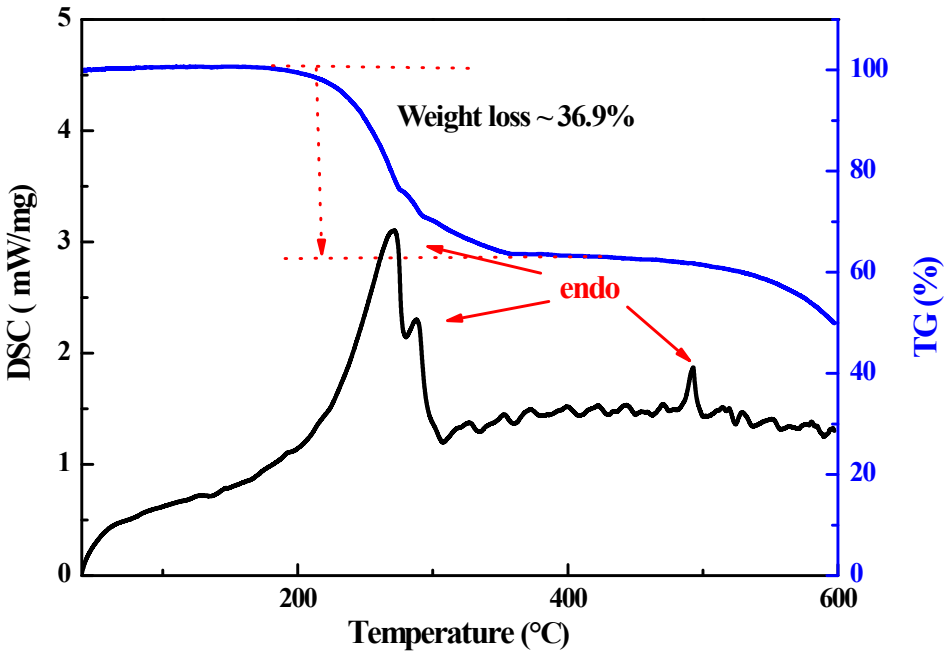

Figure S7. Electron localization function diagram of the [Pb-Cl] polyhedra in $(NH_4)_3PbCl_5$.