Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

$APb_2(C_7H_3NO_4)_2I$ (A=K, Rb, Cs): Rare Stable Nonlinear Optical Crystals with Second-Harmonic Generation Response and Highly Distorted Lead Core Coordination Polyhedra

Zi-Long Geng,[a,c] Zi-Qi Zhou,[a] Hong-Xin Tang,[a,c] Wen-Xiu Bao,[a,d] Rui-Biao Fu,[*,a,b] and Xin-Tao Wu[a]

a. State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China

b. Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, Fujian 350108

c. University of Chinese Academy of Sciences, Beijing, 100049, P. R. China E-mail: furb@fjirsm.ac.cn.

*Corresponding authors, E-mail: furb@fjirsm.ac.cn

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1. Experimental Procedures

Reagents.

Lead oxide (PbO, 98%), potassium iodide (KI, 98%) and acetic acid (CH_3COOH, 98%) were purchased from Aladdin Chemical Industry Co. Ltd. 2,6-Pyridinedicarboxylic acid ($C_7H_5NO_4$, 99%) and ethanol (EtOH, 98%) were obtained from Sinopharm Reagent and used as received.

Synthesis.

Single crystals of **$APb_2(C_7H_3NO_4)_2I$ (A=K, Rb, Cs)** were synthesized by a mix-solvothermal method (**Fig. S1**). Their yields based on PbO are more than 80%.

The synthesis of **$KPb_2(C_7H_3NO_4)_2I$.** A mixture of $C_7H_5NO_4$ (83.56 mg, 0.50 mmol), PbO (115.0 mg, 0.51 mmol), KI (60 mg, 0.36 mmol), EtOH (2 ml) and CH_3COOH (2 ml) was added into the Teflon-lined stainless-steel autoclaves and heated to 120 °C for 3 days and gradually cooled to 20 °C at a rate of 2 °C/h. The products were washed by ethanol. Massive colorless crystals of **$K[Pb_2(C_7H_3NO_4)_2I]$** were obtained. Energy dispersive X-ray spectroscope (EDS) verifies the coexistence of C, N, O, K, I and Pb (**Fig. S3**). The atomic ratio of K:I:Pb is 1.05:1.07:2.13 which is in good agreeement of the theoretical value of 1:1:2. Anal. Calcd. for **$KPb_2(C_7H_3NO_4)_2I$**: C 18.45, H 0.66, N 3.07 %. Found: C 18.77, H 0.88, N 2.82 %.

The synthesis of **$RbPb_2(C_7H_3NO_4)_2I$.** A mixture of $C_7H_5NO_4$ (101.0 mg, 0.60 mmol), PbO (111.5 mg, 0.50 mmol), RbI (64 mg, 0.30 mmol), EtOH (2 ml) and CH_3COOH (1.8 ml) was added into the Teflon-lined stainless-steel autoclaves and heated to 120 °C for 3 days and gradually cooled to 20 °C at a rate of 2 °C/h. The products were washed by ethanol. Massive colorless crystals of **$Rb[Pb_2(C_7H_3NO_4)_2I]$** were obtained. EDS verifies the coexistence of C, N, O, Rb, I and Pb. The atomic ratio of Rb:I:Pb is 0.93:1.00:1.76 which is in agreeement of the theoretical value of 1:1:2. Anal. Calcd. for **$RbPb_2(C_7H_3NO_4)_2I$:** C 17.56, H 0.63, N 2.93 %. Found: C 17.89, H 0.86, N 2.71 %.

The synthesis of **$CsPb_2(C_7H_3NO_4)_2I$.** A mixture of $C_7H_5NO_4$ (83.56 mg, 0.50 mmol), PbO (100.4 mg, 0.45 mmol), CsI (78 mg, 0.30 mmol), EtOH (2 ml) and CH_3COOH (1.8 ml) was added into the Teflon-lined stainless-steel autoclaves and heated to 120 °C for 3 days and gradually cooled to 20 °C at a rate of 2 °C/h. The products were washed by ethanol. Massive colorless crystals of **$Cs[Pb_2(C_7H_3NO_4)_2I]$** were obtained. EDS verifies the coexistence of C, N, O, Cs, I and Pb. The atomic ratio of Cs:I:Pb is 1.29:1.16:2.07 which is in agreeement of the theoretical value of 1:1:2.Anal. Calcd. for **$CsPb_2(C_7H_3NO_4)_2I$**: C 16.74, H 0.60, N 2.79 %. Found: C 17.09, H 0.88, N 2.53 %.

Single-Crystal X-ray Diffraction.

Single-crystal X-ray XRD data for **$APb_2(C_7H_3NO_4)_2I$ (A=K, Rb, Cs)** were collected by using graphite-monochromated Ga Kα radiation (λ(Ga−Kα) = 1.3405 Å) with a Rigaku Oxford

Diffraction. Data reduction were integrated with the program Crystal Clear version 1.30. Their structures were solved with a direct method using the SHELXT and refined by the SHELXL full-matrix least-squares program. [1-2] Their structures were checked by the PLATON[3] and no higher symmetries were suggested. Details of crystallographic data are listed in Table S1. Atomic coordinates, equivalent isotropic displacement parameters and bond valence sum (BVS) are summarized in Tables S2~S4. Anisotropic displacement parameters, bond lengths and angles (°) are summarized in Tables S5~S10, respectively. CCDC 2190517 for **$KPb_2(C_7H_3NO_4)_2I$**, 2190518 for **$RbPb_2(C_7H_3NO_4)_2I$** and 2190519 for **$CsPb_2(C_7H_3NO_4)_2I$**.

Powder X-ray Diffraction.

Powder XRD pattern was collected at room temperature using a Rigaku Miniflex 600 diffractometer with Cu Kα radiation (λ =1.540598 Å). Powder XRD data were obtained in the 2θ range of 5-55° with a step width of 0.02° (**Fig. S2**).

Thermal Analysis.

Thermogravimetric analysis (TGA) was performed on a NETZCH STA 449F3 thermal analysis instrument at a heating rate of 10 $^oC \cdot min^{-1}$ in a flowing nitrogen atmosphere from 30 to 800 ^oC (**Fig. S4**).

Elemental Analyses.

Elemental analyses were performed by using a field emission scanning electron microscope (FESEM, JSM6700F) with an energy dispersive X-ray spectroscope (EDS, Oxford INCA). The result shows that the product contains C, N, O, K/Rb/Cs, I and Pb (**Fig. S3**). C, H and N analyses were carried out with a Vario EL III element analyzer.

IR Spectroscopy.

IR spectrum were performed at room temperature on a VERTEX70 FT-IR spectrometer instrument by using Attenuated Total Reflectance (ATR) method and data were collected from 4000 to 400 cm^{-1}. The sample was tightly fitted to the total reflection crystal (**Fig. S6**).

UV–Vis–NIR Diffuse Reflectance Spectroscopy.

UV–Vis–NIR Diffuse Reflectance spectra were recorded at room temperature on a PrkinElmer Lambda 950 spectrophotometer using $BaSO_4$ as the standard reference. The spectral range of measurement is 200-2500 nm (**Fig. S7**). The reflection spectrum was calculated into the absorption spectrum by using the Kubelka-Munk function.[4]

SHG Test.

Powder SHG measurement was performed on a pulsed Q-switched Nd: YAG solid-state laser using the Kurtz-Perry method with a wavelength of 1064 nm at room temperature. [5] Crystalline samples and microcrystalline KDP were used as reference samples for grinding and SHG response in the particle size range of 25-45 μm.

2. Tables and Figures

Table S1. Crystal data and structure refinements for **$KPb_2(C_7H_3NO_4)_2I$**, **$RbPb_2(C_7H_3NO_4)_2I$** and **$CsPb_2(C_7H_3NO_4)_2I$**.

Empirical formula	**$KPb_2(C_7H_3NO_4)_2I$**	**$RbPb_2(C_7H_3NO_4)_2I$**	**$CsPb_2(C_7H_3NO_4)_2I$**
Formula weight	910.59	956.56	1003.39
Temperature(K)	293(2)	293(2)	100
Crystal color	Colorless	Colorless	Colorless
Wavelength(Å)	1.34050	1.34050	1.34050
Crystal system	Cubic	Cubic	Cubic
Space group	*I-43d*	*I-43d*	*I-43d*
a / Å	28.8816(1)	29.00303(7)	28.93941(4)
b / Å	28.8816(1)	29.00303(7)	28.93941(4)
c / Å	28.8816(1)	29.00303(7)	28.93941(4)
Volume / $Å^3$	24091.5(3)	24396.63(18)	24236.46(10)
Z, ρ_{calcd} / $g \cdot cm^{-3}$	48,3.013	48,3.126	48,3.300
μ / mm^{-1}	31.451	31.741	39.581
F(000)	19392.0	20256.0	21120.0
Date / restraints / parameters	3948 / 48 / 229	3439 / 84 / 241	3410 / 108 / 230
Theta range for data collection	3.259 to 55.794	3.245 to 52.040	3.252 to 52.012
Limiting indices	$-34 \le h \le 35$, $-35 \le k \le 35$, $-31 \le l \le 35$	$-26 \le h \le 34$, $-34 \le k \le 33$, $-31 \le l \le 34$	$-33 \le h \le 34$, $-34 \le k \le 34$, $-34 \le l \le 34$
Reflections collected / unique	3948 [R_{int} = 0.1018, R_{sigma}=0.0182]	3439 [R_{int} = 0.0398, R_{sigma}=0.0110]	3410 [R_{int} = 0.0421, R_{sigma}=0.0071]
Completeness	99.3%	99.3%	98.5%
Goodness-of-fit on F^2	1.059	1.059	1.050
R_1,wR_2 ($I > 2\sigma$) [a]	R_1=0.0424, R_2=0.1113	R_1=0.0460, R2=0.1152	R_1=0.0560, R2=0.1488
R_1,wR_2 (all data)	R_1=0.0426, R_2=0.1115	R_1=0.0462, R2=0.1153	R_1=0.0562, R2=0.1492
Largest diff ,peak and hole/ $Å^{-3}$	2.03 and -1.77	1.68 and -1.85	3.11 and -3.25
Flack parameter	0.022(16)	0.032(11)	0.049(7)

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(Fo^2 - Fc^2)^2/ \Sigma w\, F_o^4]^{1/2}$.

Table S2. Atomic coordinates, equivalent isotropic displacement parameters (Å^2) and BVS of **$KPb_2(C_7H_3NO_4)_2I$**.

Atom	*Wyck.*	*x*	*y*	*z*	U_{eq}[a]	BVS[b]
Pb1	48e	0.18682(4)	0.32506(3)	0.43764(3)	0.0554(3)	2.02
Pb2	48e	0.05385(3)	0.32227(3)	0.32013(2)	0.0390(2)	1.84
I1	48e	0.06907(5)	0.21000(5)	0.30611(5)	0.0485(3)	-0.40
K1	48e	0.2936(3)	0.4367(3)	0.4387(3)	0.094(2)	0.89
O1	48e	0.1523(5)	0.2466(5)	0.4356(6)	0.059(4)	-1.98
O2	48e	0.1584(6)	0.1715(5)	0.4410(7)	0.063(4)	-1.93
O3	48e	0.2720(8)	0.3464(7)	0.4450(9)	0.087(6)	-1.83
O4	48e	0.3486(9)	0.3255(9)	0.4429(9)	0.101(7)	-1.42
O5	48e	0.2096(4)	0.3187(5)	0.3573(5)	0.052(3)	-1.85
O6	48e	0.1344(5)	0.3276(6)	0.3604(5)	0.057(4)	-1.88
O7	48e	0.0380(4)	0.3253(6)	0.2373(4)	0.051(3)	-2.17
O8	48e	0.0637(12)	0.3227(11)	0.1666(12)	0.126(9)	-1.90
N1	48e	0.2430(4)	0.2594(3)	0.4402(4)	0.042(3)	
N2	48e	0.1245(3)	0.3213(4)	0.2703(3)	0.037(3)	
C1	48e	0.1752(7)	0.2095(7)	0.4393(7)	0.044(4)	
C2	48e	0.2264(3)	0.2142(3)	0.4389(4)	0.042(4)	
C3	48e	0.2572(4)	0.1773(3)	0.4372(5)	0.051(5)	
C4	48e	0.3047(4)	0.1855(4)	0.4368(5)	0.053(5)	
C5	48e	0.3213(3)	0.2307(4)	0.4382(5)	0.060(6)	
C6	48e	0.2905(4)	0.2676(3)	0.4399(4)	0.045(4)	
C7	48e	0.3045(11)	0.3163(10)	0.4443(10)	0.072(7)	
C8	48e	0.1702(6)	0.3223(7)	0.3388(6)	0.040(4)	
C9	48e	0.1690(4)	0.3211(4)	0.2887(3)	0.038(4)	
C10	48e	0.2071(3)	0.3215(5)	0.2594(5)	0.056(5)	
C11	48e	0.2008(4)	0.3221(6)	0.2116(4)	0.060(6)	
C12	48e	0.1563(4)	0.3223(6)	0.1933(3)	0.068(7)	
C13	48e	0.1181(3)	0.3219(5)	0.2226(3)	0.050(5)	
C14	48e	0.0678(8)	0.3205(8)	0.2082(8)	0.054(5)	

[a]U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

[b]Bond valence sums were calculated by the equation：$s = \exp[(R_0 - R_i)/b]$, where R_0 and b are the bond valence parameters and R_i is the observed bond lengths.

Table S3. Atomic coordinates, equivalent isotropic displacement parameters (Å^2) and BVS of **$RbPb_2(C_7H_3NO_4)_2I$**.

Atom	*Wyck.*	*x*	*y*	*z*	U_{eq}[a]	BVS[b]
Pb1	48e	0.32185(4)	0.31972(3)	0.05466(3)	0.0499(3)	1.86
Pb2	48e	0.32403(3)	0.43671(4)	0.18485(5)	0.0735(4)	2.04
I1	48e	0.20985(6)	0.30756(5)	0.06903(6)	0.0582(4)	-0.42
Rb1	48e	0.3107(3)	0.18546(16)	-0.04669(18)	0.156(3)	0.73
O1	48e	0.3202(10)	0.1661(8)	0.0643(10)	0.101(7)	-1.90
O2	48e	0.3245(7)	0.2364(5)	0.0395(6)	0.063(5)	-2.16
O3	48e	0.3174(6)	0.3578(7)	0.2101(6)	0.068(5)	-1.79
O4	48e	0.3262(8)	0.3596(7)	0.1344(7)	0.074(5)	-2.03
O5	48e	0.4069(7)	0.3113(8)	0.0798(6)	0.071(5)	-1.94
O6	48e	0.2457(5)	0.4352(7)	0.1513(7)	0.070(5)	-2.06
O7	48e	0.3454(8)	0.4464(10)	0.2678(9)	0.104(7)	-2.05
O8	48e	0.3266(10)	0.4507(11)	0.3440(10)	0.120(9)	-1.39
N1	48e	0.3209(5)	0.2700(4)	0.1247(4)	0.046(4)	
N2	48e	0.4927(7)	0.3092(7)	-0.0085(6)	0.053(5)	
C1	48e	0.3222(9)	0.2076(9)	0.0694(10)	0.061(6)	
C2	48e	0.3215(6)	0.2224(4)	0.1190(4)	0.051(5)	
C3	48e	0.3220(7)	0.1936(4)	0.1573(5)	0.078(9)	
C4	48e	0.3218(7)	0.2124(5)	0.2014(4)	0.077(8)	
C5	48e	0.3212(6)	0.2600(6)	0.2072(3)	0.063(6)	
C6	48e	0.3207(5)	0.2888(4)	0.1688(5)	0.052(6)	
C7	48e	0.3222(8)	0.3384(8)	0.1707(8)	0.050(5)	
C8	48e	0.4219(10)	0.3088(7)	0.0413(7)	0.053(6)	
C9	48e	0.4764(10)	0.3121(8)	0.0352(8)	0.058(6)	
C10	48e	0.5068(8)	0.3132(8)	0.0725(8)	0.051(5)	
C11	48e	0.5508(8)	0.3103(9)	0.0642(8)	0.056(6)	
C12	48e	0.3166(13)	0.4464(13)	0.2998(13)	0.086(9)	
C13	48e	0.2672(8)	0.4402(8)	0.2880(9)	0.053(5)	
C14	48e	0.2316(8)	0.4396(8)	0.3171(10)	0.060(6)	

[a]U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

[b]Bond valence sums were calculated by the equation：$s = \exp[(R_0 - R_i)/b]$, where R_0 and b are the bond valence parameters and R_i is the observed bond lengths.

Table S4. Atomic coordinates, equivalent isotropic displacement parameters (Å^2) and BVS of **$CsPb_2(C_7H_3NO_4)_2I$**.

Atom	*Wyck.*	*x*	*y*	*z*	U_{eq}[a]	BVS[b]
Pb1	48e	0.68716(5)	0.07398(4)	0.56692(6)	0.0555(4)	2.04
Pb2	48e	0.68049(3)	-0.05494(4)	0.67905(4)	0.0358(3)	1.88
I1	48e	0.69155(6)	-0.06929(6)	0.79035(6)	0.0394(5)	-0.53
Cs1	48e	0.8154(2)	-0.0527(3)	0.8119(4)	0.212(4)	1.17
O1	48e	0.7054(10)	0.0794(10)	0.4091(9)	0.072(7)	-1.78
O2	48e	0.6948(12)	0.0958(9)	0.4839(10)	0.079(7)	-2.31
O3	48e	0.6859(7)	-0.0043(6)	0.6005(7)	0.045(4)	-1.82
O4	48e	0.6906(7)	-0.0796(7)	0.5922(7)	0.044(5)	-1.92
O5	48e	0.6101(8)	0.0758(9)	0.6163(7)	0.061(6)	-1.90
O6	48e	0.6072(7)	0.0676(7)	0.5392(6)	0.044(4)	-1.93
O7	48e	0.4861(6)	0.0741(7)	0.7102(6)	0.041(4)	-2.10
O8	48e	0.4151(8)	0.0764(11)	0.6859(10)	0.070(7)	-1.95
N1	48e	0.6913(6)	0.0085(4)	0.5101(5)	0.043(5)	
N2	48e	0.5196(5)	0.0713(6)	0.6248(4)	0.037(5)	
C1	48e	0.6923(14)	0.0715(14)	0.4495(15)	0.065(9)	
C2	48e	0.6909(6)	0.0177(4)	0.4630(5)	0.036(5)	
C3	48e	0.6882(6)	-0.0184(5)	0.4314(4)	0.041(6)	
C4	48e	0.6860(6)	-0.0638(4)	0.4471(5)	0.034(5)	
C5	48e	0.6864(6)	-0.0730(4)	0.4942(5)	0.038(6)	
C6	48e	0.6891(6)	-0.0368(5)	0.5257(4)	0.039(6)	
C7	48e	0.6875(12)	-0.0420(9)	0.5753(11)	0.043(7)	
C8	48e	0.5893(11)	0.0712(11)	0.5778(11)	0.046(7)	
C9	48e	0.5385(5)	0.0697(7)	0.5807(7)	0.040(6)	
C10	48e	0.5098(7)	0.0706(8)	0.5422(4)	0.056(8)	
C11	48e	0.4621(6)	0.0731(9)	0.5478(5)	0.064(9)	
C12	48e	0.4432(4)	0.0747(8)	0.5919(7)	0.049(7)	
C13	48e	0.4720(5)	0.0738(7)	0.6304(5)	0.047(7)	
C14	48e	0.4561(9)	0.0741(10)	0.6800(10)	0.037(6)	

[a]U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

[b]Bond valence sums were calculated by the equation: $s = \exp[(R_0 - R_i)/b]$, where R_0 and b are the bond valence parameters and R_i is the observed bond lengths.

Table S5. Anisotropic displacement parameters (Å^2) of **$KPb_2(C_7H_3NO_4)_2I$**.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb1	0.0872(6)	0.031.1(4)	0.0480(4)	0.0123(4)	-0.0117(4)	-0.0045(3)
Pb2	0.0337(3)	0.053.4(4)	0.0300(3)	-0.0030(3)	0.0027(2)	0.0032(3)
I1	0.0434(6)	0.056.4(7)	0.0457(6)	0.0018(5)	-0.0037(6)	0.0022(5)
K1	0.092(2)	0.092(2)	0.097(2)	-0.0003(14)	-0.0032(14)	-0.0034(14)
O1	0.063(9)	0.033(7)	0.082(11)	0.011(6)	-0.001(8)	-0.007(7)
O2	0.064(9)	0.032(7)	0.093(13)	0.004(7)	-0.001(9)	0.009(8)
O3	0.093(10)	0.061(9)	0.107(11)	-0.005(8)	-0.023(10)	-0.018(9)
O4	0.101(7)	0.101(7)	0.101(7)	-0.0003(14)	-0.0002(14)	0.0001(14)
O5	0.036(7)	0.064(9)	0.056(8)	0.007(6)	-0.020(6)	0.004(7)
O6	0.048(8)	0.084(11)	0.039(7)	-0.008(8)	-0.014(6)	0.008(7)
O7	0.034(6)	0.082(10)	0.035(7)	-0.002(7)	-0.003(5)	0.003(7)
O8	0.126(9)	0.127(9)	0.126(9)	0.0001(14)	0.0000(15)	-0.0001(14)
N1	0.067(10)	0.028(7)	0.031(7)	0.003(6)	-0.014(7)	0.000(6)
N2	0.037(7)	0.044(8)	0.030(7)	-0.005(6)	0.002(5)	0.008(6)
C1	0.052(10)	0.040(10)	0.040(10)	0.004(8)	0.010(8)	0.008(7)
C2	0.072(13)	0.022(7)	0.031(8)	0.005(8)	-0.007(8)	0.003(6)
C3	0.068(13)	0.032(9)	0.053(11)	0.003(9)	0.001(10)	0.008(8)
C4	0.048(11)	0.029(9)	0.084(16)	0.009(8)	-0.013(11)	-0.014(9)
C5	0.066(13)	0.060(13)	0.053(12)	-0.022(11)	-0.016(11)	0.011(10)
C6	0.049(10)	0.048(10)	0.039(10)	-0.004(8)	-0.016(8)	-0.005(8)
C7	0.072(7)	0.072(7)	0.073(7)	-0.0002(14)	-0.0004(14)	0.0000(14)
C8	0.040(4)	0.039(4)	0.040(4)	0.0004(14)	-0.0006(14)	0.0000(14)
C9	0.035(8)	0.033(9)	0.045(9)	-0.006(7)	0.005(7)	0.005(7)
C10	0.045(11)	0.053(12)	0.070(14)	-0.006(9)	0.012(10)	0.009(11)
C11	0.033(10)	0.080(16)	0.067(14)	-0.011(10)	0.019(9)	-0.017(13)
C12	0.050(12)	0.110(20)	0.046(11)	-0.002(13)	0.024(9)	-0.013(13)
C13	0.057(12)	0.062(13)	0.033(9)	-0.002(10)	0.005(8)	-0.001(9)
C14	0.054(5)	0.055(5)	0.054(5)	-0.0001(14)	0.0001(14)	-0.0004(14)

Table S6. Anisotropic displacement parameters (Å^2) of **$RbPb_2(C_7H_3NO_4)_2I$**.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb1	0.0693(6)	0.0358(4)	0.0445(5)	0.0028(4)	-0.0089(4)	0.0001(3)
Pb2	0.0372(5)	0.0623(7)	0.1212(11)	-0.0105(4)	0.0216(6)	-0.0346(7)
I1	0.0717(10)	0.0479(8)	0.0549(9)	-0.0008(7)	-0.0007(7)	-0.0046(7)
Rb1	0.277(7)	0.083(2)	0.109(3)	0.025(3)	-0.107(4)	-0.006(2)
O1	0.137(13)	0.068(10)	0.098(12)	-0.018(10)	0.008(11)	-0.013(10)
O2	0.106(14)	0.028(7)	0.054(9)	0.020(8)	-0.021(9)	-0.015(7)
O3	0.059(11)	0.084(12)	0.063(11)	0.008(9)	0.009(8)	-0.029(9)
O4	0.095(11)	0.062(9)	0.065(9)	0.003(8)	-0.014(9)	-0.011(8)
O5	0.076(12)	0.093(15)	0.043(10)	-0.011(11)	-0.013(9)	0.004(9)
O6	0.038(8)	0.083(13)	0.088(13)	-0.014(9)	0.027(8)	-0.013(11)
O7	0.080(11)	0.123(13)	0.109(12)	-0.018(10)	0.007(10)	-0.031(11)
O8	0.109(13)	0.135(14)	0.115(13)	-0.002(11)	-0.023(11)	-0.033(11)
N1	0.050(11)	0.047(10)	0.041(9)	0.002(8)	0.001(8)	0.006(8)
N2	0.076(10)	0.048(9)	0.033(7)	0.018(8)	-0.011(7)	-0.005(7)
C1	0.068(11)	0.045(10)	0.070(12)	-0.005(9)	-0.011(10)	-0.001(10)
C2	0.060(14)	0.039(11)	0.054(13)	-0.005(10)	-0.001(10)	0.007(10)
C3	0.12(3)	0.050(14)	0.064(17)	-0.011(16)	-0.034(17)	0.039(12)
C4	0.078(13)	0.085(13)	0.068(12)	0.003(11)	-0.013(10)	0.016(11)
C5	0.063(6)	0.064(6)	0.063(6)	0.0001(15)	-0.0001(15)	0.0000(15)
C6	0.043(12)	0.076(16)	0.038(12)	0.013(11)	0.001(9)	0.005(10)
C7	0.044(9)	0.058(10)	0.048(10)	0.004(9)	0.004(8)	-0.009(9)
C8	0.100(19)	0.031(11)	0.029(11)	0.005(11)	-0.006(12)	-0.001(8)
C9	0.087(18)	0.035(11)	0.052(13)	0.026(12)	-0.009(12)	0.013(10)
C10	0.063(10)	0.044(9)	0.046(9)	-0.004(8)	-0.001(8)	0.000(8)
C11	0.046(10)	0.070(11)	0.053(10)	0.016(9)	0.012(9)	-0.003(9)
C12	0.082(14)	0.100(14)	0.076(13)	-0.007(12)	-0.006(11)	-0.027(11)
C13	0.041(9)	0.050(10)	0.068(11)	-0.010(8)	-0.002(8)	-0.029(9)
C14	0.056(13)	0.046(12)	0.077(17)	0.012(11)	-0.002(11)	-0.014(12)

Table S7. Anisotropic displacement parameters (Å^2) of **$CsPb_2(C_7H_3NO_4)_2I$**.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb1	0.0585(8)	0.0283(6)	0.0796(10)	-0.0130(6)	0.0219(7)	-0.0042(5)
Pb2	0.0277(5)	0.0285(5)	0.0512(7)	-0.0055(4)	0.0019(4)	-0.0014(4)
I1	0.0296(8)	0.0335(8)	0.0550(11)	0.0008(7)	-0.0028(7)	-0.0016(7)
Cs1	0.124(4)	0.163(5)	0.350(10)	-0.087(6)	-0.027(5)	0.009(4)
O1	0.085(13)	0.064(11)	0.068(12)	-0.004(10)	0.024(10)	-0.006(10)
O2	0.102(13)	0.060(11)	0.075(12)	-0.005(10)	0.029(11)	-0.003(10)
O3	0.049(9)	0.035(8)	0.052(9)	-0.009(7)	0.006(8)	-0.008(7)
O4	0.053(10)	0.044(9)	0.034(8)	-0.010(7)	-0.005(8)	-0.004(8)
O5	0.073(15)	0.080(17)	0.028(10)	0.012(10)	0.015(10)	0.013(13)
O6	0.064(10)	0.037(9)	0.033(8)	-0.001(7)	0.013(7)	0.000(8)
O7	0.026(9)	0.059(12)	0.038(10)	0.015(9)	0.005(7)	0.010(8)
O8	0.043(10)	0.101(13)	0.067(11)	0.011(10)	0.008(9)	-0.008(10)
N1	0.034(10)	0.035(9)	0.060(11)	-0.010(8)	0.011(9)	0.003(8)
N2	0.038(11)	0.052(14)	0.020(9)	-0.003(9)	0.001(8)	-0.002(10)
C1	0.067(14)	0.061(14)	0.067(14)	-0.005(11)	0.024(12)	-0.002(12)
C2	0.041(11)	0.028(10)	0.039(10)	0.001(8)	0.018(9)	-0.006(9)
C3	0.034(13)	0.029(12)	0.060(17)	0.004(12)	0.021(13)	0.005(10)
C4	0.035(5)	0.034(5)	0.035(5)	0.0001(15)	0.0004(15)	0.0001(15)
C5	0.030(12)	0.034(13)	0.049(15)	0.002(11)	-0.012(11)	0.005(11)
C6	0.027(10)	0.036(10)	0.055(12)	-0.013(9)	0.004(9)	0.011(9)
C7	0.058(18)	0.020(12)	0.051(16)	0.001(11)	-0.008(14)	0.016(12)
C8	0.051(12)	0.037(11)	0.050(12)	0.002(10)	0.006(10)	0.005(10)
C9	0.061(17)	0.032(14)	0.026(13)	0.008(11)	-0.002(12)	0.002(12)
C10	0.065(13)	0.055(13)	0.047(12)	0.004(10)	-0.009(10)	0.004(11)
C11	0.069(14)	0.054(13)	0.068(14)	0.005(11)	-0.021(11)	0.005(11)
C12	0.043(11)	0.055(12)	0.050(12)	0.002(10)	-0.020(10)	-0.003(10)
C13	0.062(18)	0.037(15)	0.042(15)	0.015(12)	0.006(14)	-0.001(13)
C14	0.026(10)	0.041(11)	0.044(11)	0.010(9)	-0.005(9)	0.004(9)

Table S8. Selected bond lengths (Å) and angles (deg.) for **$KPb_2(C_7H_3NO_4)_2I$**.

Pb(1)-O(1)	2.475(15)	Pb(2)-O(1)$^{\#2}$	2.738(16)
Pb(1)-O(3)	2.55(2)	Pb(2)-O(2)$^{\#2}$	2.607(17)
Pb(1)-O(5)	2.419(15)	Pb(2)-O(6)	2.606(13)
Pb(1)-O(6)	2.697(13)	Pb(2)-O(7)	2.438(13)
Pb(1)-O(8)$^{\#1}$	2.66(3)	Pb(2)-N(2)	2.496(8)
Pb(1)-N(1)	2.498(8)	Pb(2)-I(1)	3.2971(16)
O(1)-Pb(1)-O(3)	127.8(6)	O(1)$^{\#2}$-Pb(2)-O(2)$^{\#2}$	48.1(4)
O(1)-Pb(1)-O(5)	91.0(5)	O(1)$^{\#2}$-Pb(2)-O(6)	116.9(5)
O(1)-Pb(1)-O(6)	77.2(6)	O(1)$^{\#2}$-Pb(2)-O(7)	79.1(5)
O(1)-Pb(1)-O(8)$^{\#1}$	154.7(8)	O(1)$^{\#2}$-Pb(2)-N(2)	114.2(4)
O(1)-Pb(1)-N(1)	64.4(4)	O(1)$^{\#2}$-Pb(2)-I(1)	153.3(3)
O(3)-Pb(1)-O(5)	80.5(7)	O(2)$^{\#2}$-Pb(2)-O(6)	75.9(5)
O(3)-Pb(1)-O(6)	127.2(7)	O(2)$^{\#2}$-Pb(2)-O(7)	84.0(6)
O(3)-Pb(1)-O(8)$^{\#1}$	76.9(9)	O(2)$^{\#2}$-Pb(2)-N(2)	73.5(4)
O(3)-Pb(1)-N(1)	63.5(5)	O(2)$^{\#2}$-Pb(2)-I(1)	152.5(3)
O(5)-Pb(1)-O(6)	50.3(4)	O(6)-Pb(2)-O(7)	127.1(4)
O(5)-Pb(1)-O(8)$^{\#1}$	88.3(8)	O(6)-Pb(2)-N(2)	61.8(4)
O(5)-Pb(1)-N(1)	78.1(4)	O(6)-Pb(2)-I(1)	89.6(4)
O(6)-Pb(1)-O(8)$^{\#1}$	83.0(8)	O(7)-Pb(2)-N(2)	65.7(4)
O(6)-Pb(1)-N(1)	114.2(5)	O(7)-Pb(2)-I(1)	86.5(4)
O(8)$^{\#1}$-Pb(1)-N(1)	139.6(8)	N(2)-Pb(2)-I(1)	79.0(3)

Symmetry transformations used to generate equivalent atoms: #1 1/4 - x, 3/4 - y, 1/4 + z; #2 1/4 + x, 1/4 - y, 3/4 - z.

Table S9. Selected bond lengths (Å) and angles (deg.) for **$KPb_2(C_7H_3NO_4)_2I$**.

Pb(1)-O(2)	2.457(14)	Pb(2)-O(1)$^{\#2}$	2.68(2)
Pb(1)-O(4)	2.589(18)	Pb(2)-O(3)	2.41(2)
Pb(1)-O(5)	2.585(19)	Pb(2)-O(4)	2.673(17)
Pb(1)-O(6)$^{\#1}$	2.73(2)	Pb(2)-O(6)	2.471(18)
Pb(1)-N(1)	2.493(10)	Pb(2)-O(7)	2.50(3)
Pb(1)-I(1)	3.294(2)	Pb(2)-N(2)$^{\#3}$	2.538(18)
O(2)-Pb(1)-O(4)	126.7(6)	O(1)$^{\#2}$-Pb(2)-O(3)	90.3(8)
O(2)-Pb(1)-O(5)	85.8(7)	O(1)$^{\#2}$-Pb(2)-O(4)	85.4(8)
O(2)-Pb(1)-O(6)$^{\#1}$	80.0(6)	O(1)$^{\#2}$-Pb(2)-O(6)	156.7(7)
O(2)-Pb(1)-N(1)	64.9(5)	O(1)$^{\#2}$-Pb(2)-O(7)	75.7(8)
O(2)-Pb(1)-I(1)	87.0(5)	O(1)$^{\#2}$-Pb(2)-N(2)$^{\#3}$	138.1(8)
O(4)-Pb(1)-O(5)	75.2(7)	O(3)-Pb(2)-O(4)	51.3(6)
O(4)-Pb(1)-O(6)$^{\#1}$	117.4(6)	O(3)-Pb(2)-O(6)	91.7(6)
O(4)-Pb(1)-N(1)	62.1(5)	O(3)-Pb(2)-O(7)	80.4(8)
O(4)-Pb(1)-I(1)	89.0(5)	O(3)-Pb(2)-N(2)$^{\#3}$	77.5(6)
O(5)-Pb(1)-O(6)$^{\#1}$	48.7(5)	O(4)-Pb(2)-O(6)	77.9(7)
O(5)-Pb(1)-N(1)	74.1(5)	O(4)-Pb(2)-O(7)	128.0(8)
O(5)-Pb(1)-I(1)	153.6(4)	O(4)-Pb(2)-N(2)$^{\#3}$	114.7(6)
O(6)$^{\#1}$-Pb(1)-N(1)	114.5(5)	O(6)-Pb(2)-O(7)	127.7(7)
O(6)$^{\#1}$-Pb(1)-I(1)	153.4(3)	O(6)-Pb(2)-N(2)$^{\#3}$	64.7(6)
N(1)-Pb(1)-I(1)	79.9(3)	O(7)-Pb(2)-N(2)$^{\#3}$	62.9(7)

Symmetry transformations used to generate equivalent atoms: #1 1/4 - x, 3/4 - y, 1/4 + z; #2 3/4 - x, 1/4 + y, 1/4 - z; #3 -1/4 + x, 3/4 - y, 1/4 - z

Table S10. Selected bond lengths (Å) and angles (deg.) for **$CsPb_2(C_7H_3NO_4)_2I$**.

Pb(1)-O(2)	2.49(3)	Pb(2)-O(3)	2.71(2)
Pb(1)-O(3)	2.466(19)	Pb(2)-O(4)	2.629(18)
Pb(1)-O(5)	2.65(2)	Pb(2)-O(5)$^{\#2}$	2.569(19)
Pb(1)-O(6)	2.45(2)	Pb(2)-O(7)$^{\#2}$	2.454(17)
Pb(1)-O(8)$^{\#1}$	2.67(2)	Pb(2)-N(2)$^{\#2}$	2.49(8)
Pb(1)-N(1)	2.511(10)	Pb(2)-I(1)	3.263(2)
O(2)-Pb(1)-O(3)	127.8(8)	O(3)-Pb(2)-O(4)	48.5(6)
O(2)-Pb(1)-O(5)	126.1(9)	O(3)-Pb(2)-O(5)$^{\#2}$	117.4(7)
O(2)-Pb(1)-O(6)	77.8(9)	O(3)-Pb(2)-O(7)$^{\#2}$	79.3(7)
O(2)-Pb(1)-O(8)$^{\#1}$	74.5(9)	O(3)-Pb(2)-N(2)$^{\#2}$	113.8(18)
O(2)-Pb(1)-N(1)	63.6(7)	O(3)-Pb(2)-I(1)	153.0(4)
O(3)-Pb(1)-O(5)	78.1(8)	O(4)-Pb(2)-O(5)$^{\#2}$	76.0(7)
O(3)-Pb(1)-O(6)	92.6(6)	O(4)-Pb(2)-O(7)$^{\#2}$	84.4(6)
O(3)-Pb(1)-O(8)$^{\#1}$	156.7(8)	O(4)-Pb(2)-N(2)$^{\#2}$	73(2)
O(3)-Pb(1)-N(1)	64.3(6)	O(4)-Pb(2)-I(1)	153.9(5)
O(5)-Pb(1)-O(6)	52.0(7)	O(5)$^{\#2}$-Pb(2)-O(7)$^{\#2}$	127.3(7)
O(5)-Pb(1)-O(8)$^{\#1}$	82.7(8)	O(5)$^{\#2}$-Pb(2)-N(2)$^{\#2}$	63(2)
O(5)-Pb(1)-N(1)	114.1(7)	O(5)$^{\#2}$-Pb(2)-I(1)	89.2(6)
O(6)-Pb(1)-O(8)$^{\#1}$	85.7(8)	O(7)$^{\#2}$-Pb(2)-N(2)$^{\#2}$	65(2)
O(6)-Pb(1)-N(1)	77.0(6)	O(7)$^{\#2}$-Pb(2)-I(1)	87.9(5)
O(8)$^{\#\backslash 1}$-Pb(1)-N(1)	137.1(7)	N(2)$^{\#2}$-Pb(2)-I(1)	81(2)

Symmetry transformations used to generate equivalent atoms: #1 - 1/4 + x, 3/4 - y, 5/4 - z; #2 5/4 - x, 3/4 - y, - 5/4 + z.

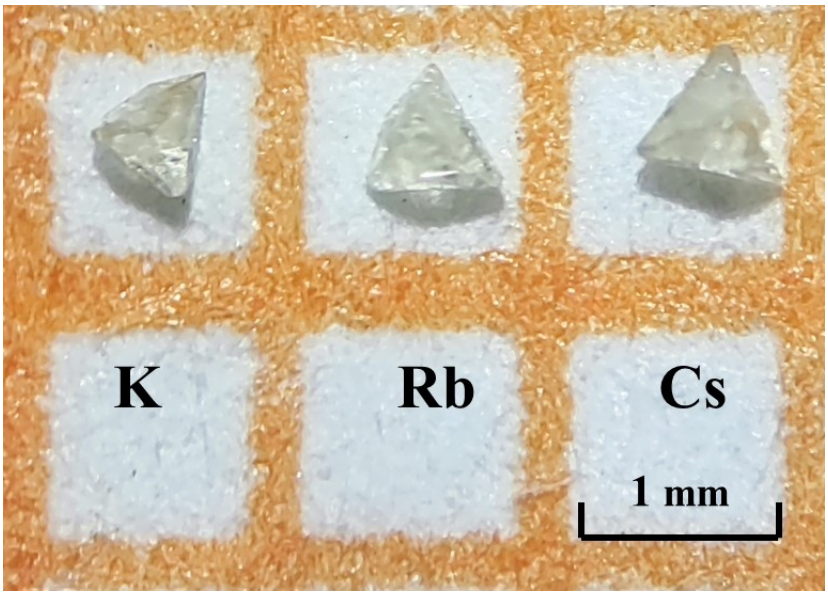


Figure S1. A Photograph of the as-grown crystals without polishing for **$KPb_2(C_7H_3NO_4)_2I$**, **$RbPb_2(C_7H_3NO_4)_2I$** and **$CsPb_2(C_7H_3NO_4)_2I$**.

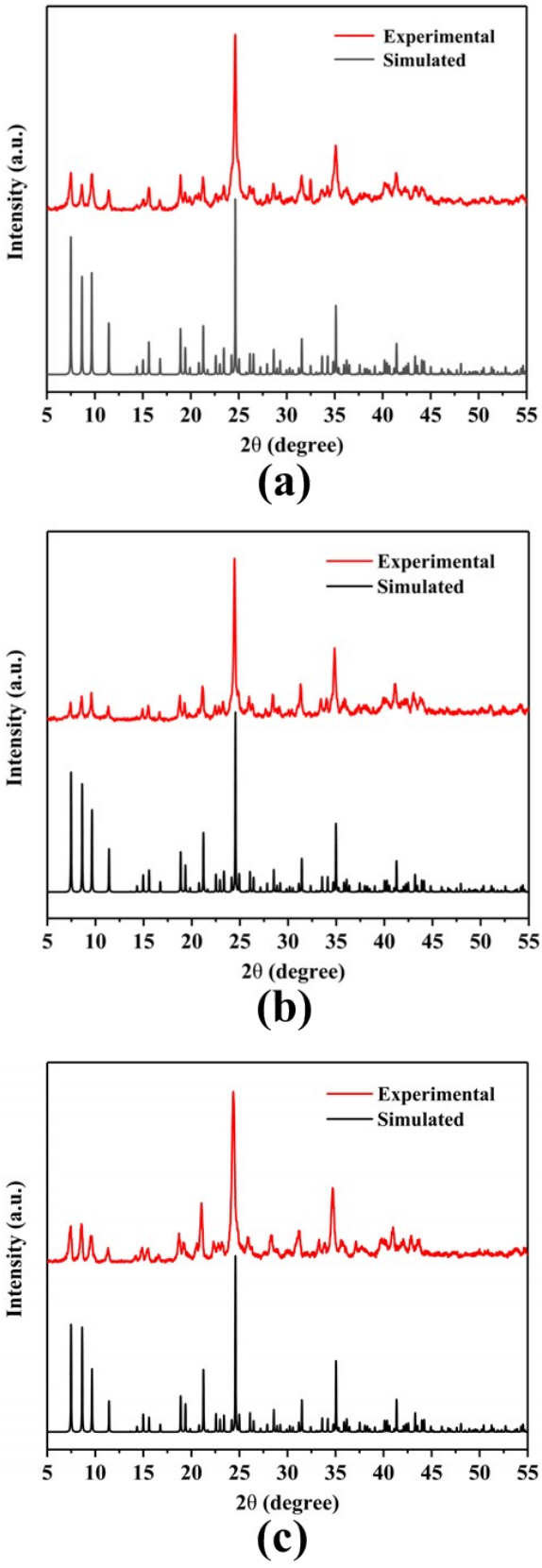
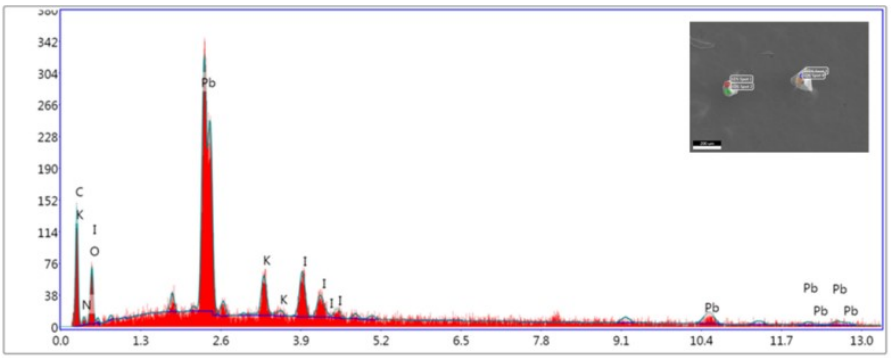


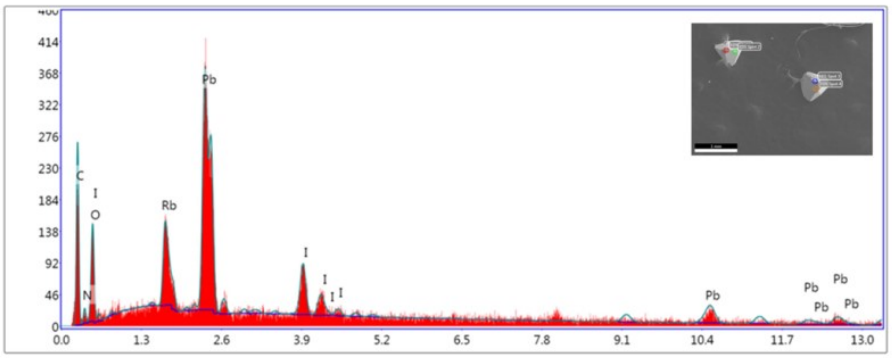
Figure S2. Experimental and simulated PXRD patterns of (a) **$KPb_2(C_7H_3NO_4)_2I$**, (b) **$RbPb_2(C_7H_3NO_4)_2I$** and (c) **$CsPb_2(C_7H_3NO_4)_2I$**.



Lsec: 20.5 0 Cnts 0.000 keV Det: Octane Plus Det

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
PbM	23.40	2.13	282.08	6.83	0.21	0.65	1.37	1.33	1.01
K K	2.17	1.05	46.84	16.29	0.02	0.94	1.01	0.82	1
I L	7.17	1.07	55.70	24.42	0.05	0.72	1.21	1.02	1

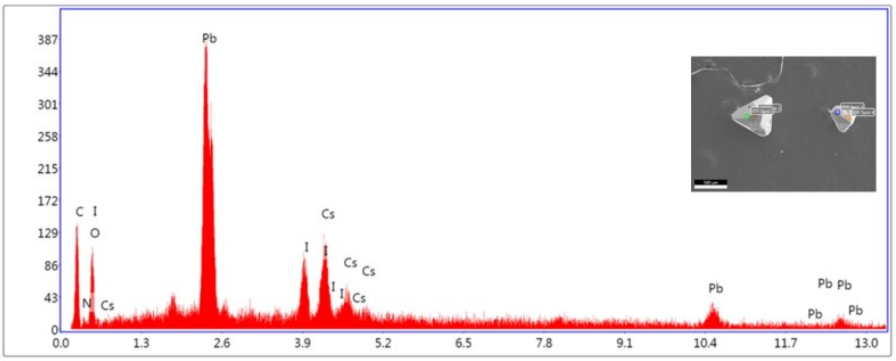
(a)



Lsec: 17.4 0 Cnts 0.000 keV Det: Octane Plus Det

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
PbM	19.66	1.76	310.15	8.45	0.16	0.65	1.38	1.28	1
RbL	4.30	0.93	88.15	8.40	0.03	0.77	1.15	0.94	1
I L	6.81	1.00	73.29	20.24	0.05	0.71	1.21	1.04	1

(b)



Lsec: 22.2 0 Cnts 0.000 keV Det: Octane Plus Det

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
PbM	21.26	2.07	336.24	7.83	0.18	0.67	1.35	1.27	1.01
CsL	8.50	1.29	81.58	20.90	0.06	0.72	1.2	1.03	1
I L	7.27	1.16	78.39	20.58	0.06	0.74	1.2	1.02	1

(c)

Figure S3. EDS spectra of (a) **$KPb_2(C_7H_3NO_4)_2I$**, (b) **$RbPb_2(C_7H_3NO_4)_2I$** and (c) **$CsPb_2(C_7H_3NO_4)_2I$**.

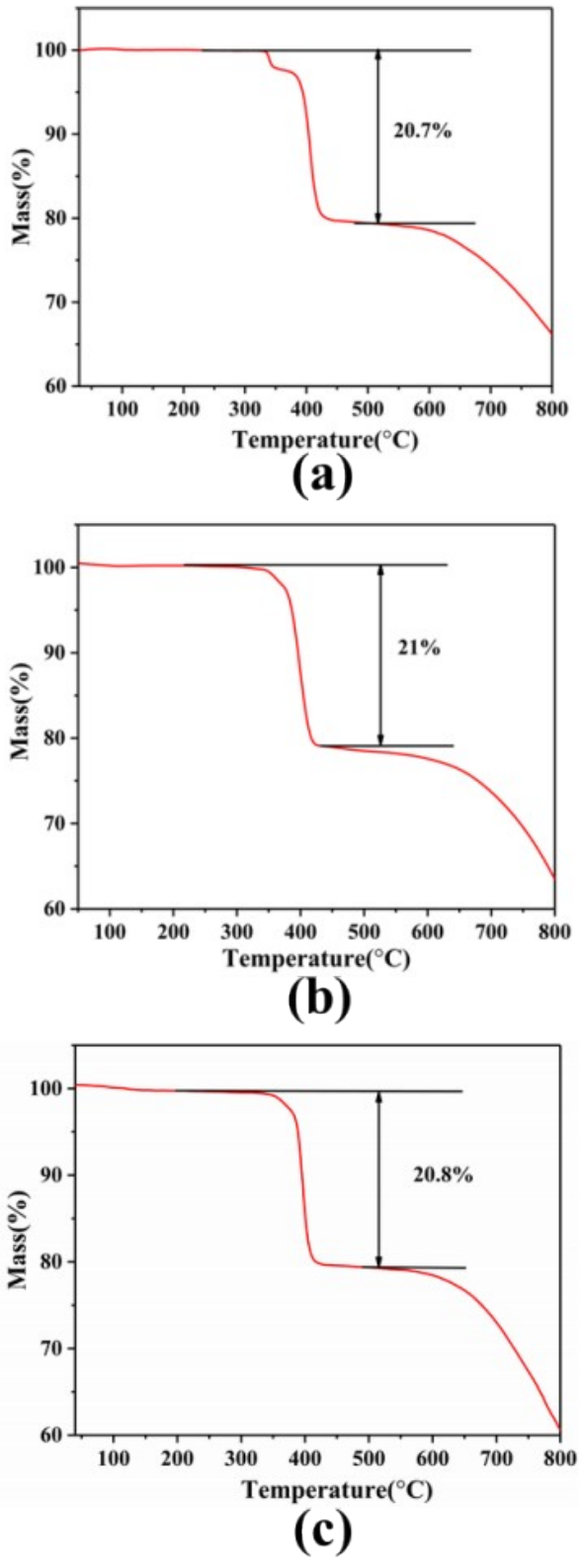
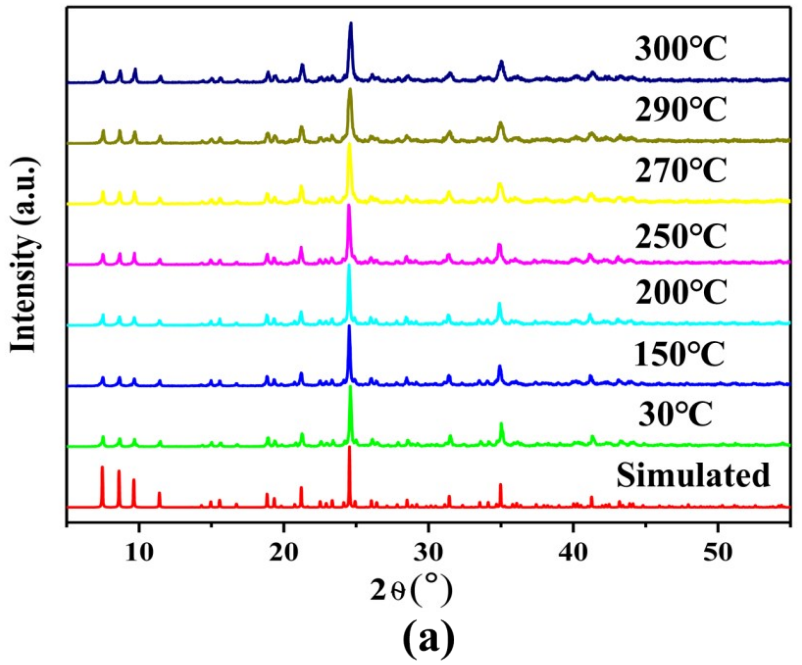


Figure S4. TG curves of (a) **$KPb_2(C_7H_3NO_4)_2I$**, (b) **$RbPb_2(C_7H_3NO_4)_2I$** and (c) **$CsPb_2(C_7H_3NO_4)_2I$**.



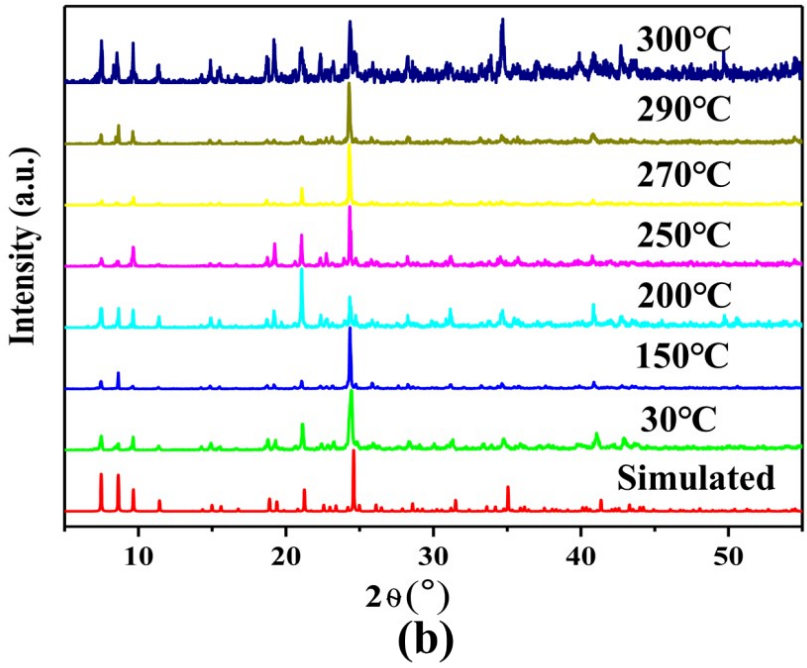


Figure S5. Variable-temperature PXRD patterns of (a) **$RbPb_2(C_7H_3NO_4)_2I$ and** (b) **$CsPb_2(C_7H_3NO_4)_2I$**.

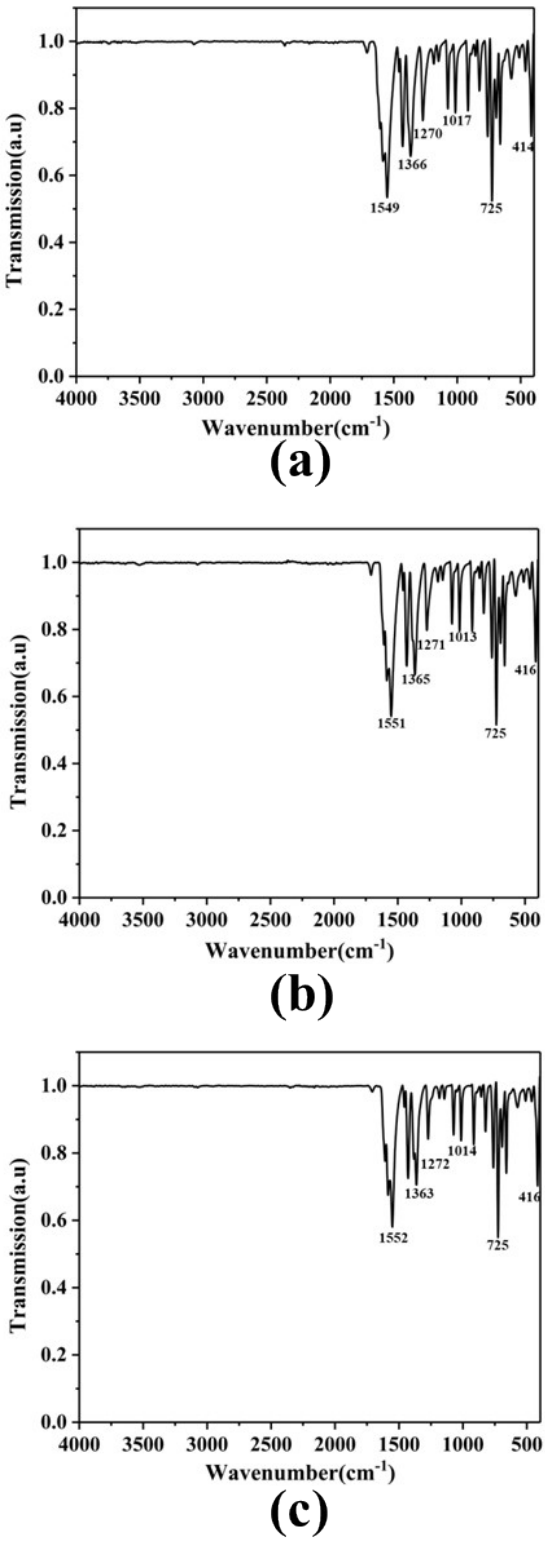
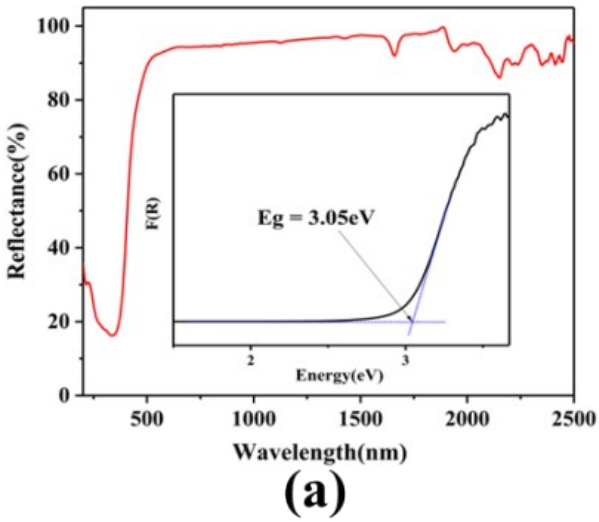
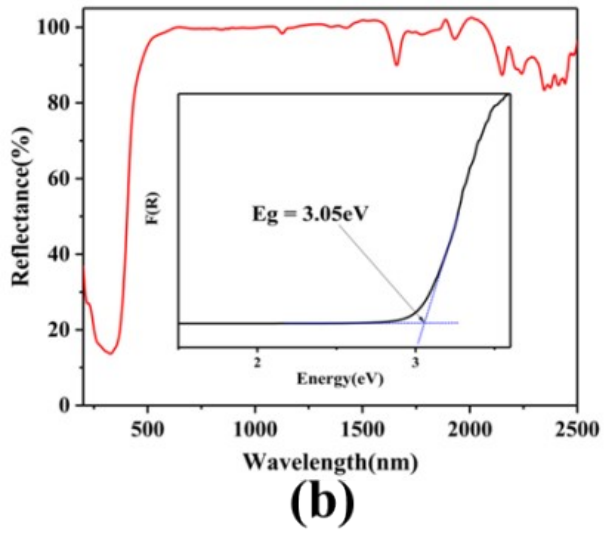


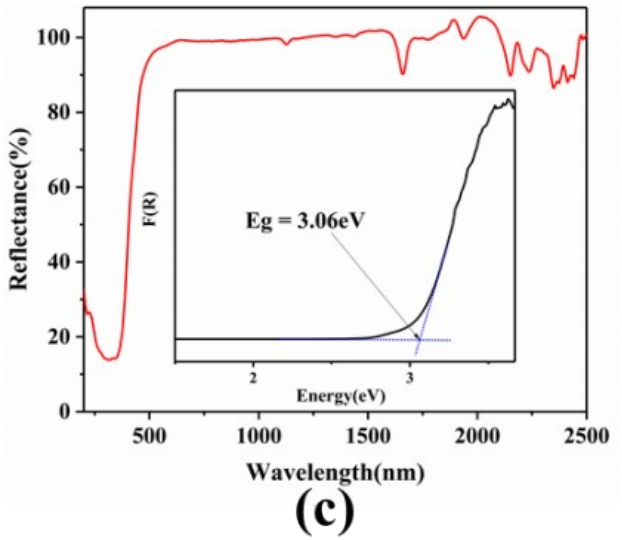
Figure S6. IR spectra of (a) $KPb_2(C_7H_3NO_4)_2I$, (b) $RbPb_2(C_7H_3NO_4)_2I$ and (c) $CsPb_2(C_7H_3NO_4)_2I$.



(a)



(b)



(c)

Figure S7. UV-Vis-NIR spectra of (a) **$KPb_2(C_7H_3NO_4)_2I$**, (b) **$RbPb_2(C_7H_3NO_4)_2I$** and (c) **$CsPb_2(C_7H_3NO_4)_2I$**.

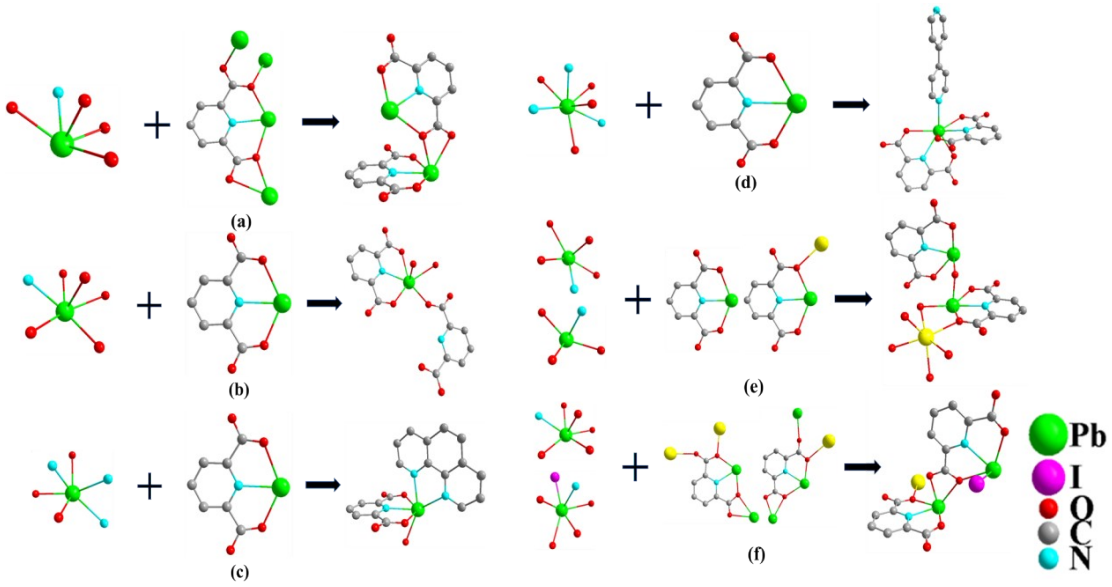


Figure S8. Lead-centered coordination polyhedra, coordination modes of 2,6-pyridinedicarboxylate group and structural units in (a) **$C_7H_3NO_4Pb$**, (b) **$C_{14}H_{14}N_2O_{11}Pb$**, (c) **$C_{19}H_{17}N_3O_8Pb$**, (d) **$C_{39}H_{36}N_7O_{12}Pb$**, (e) **$C_{14}H_{15}N_2O_{13}NaPb_2$** and (f) **$APb_2(C_7H_3NO_4)_2I$ (A=K, Rb, Cs)**.

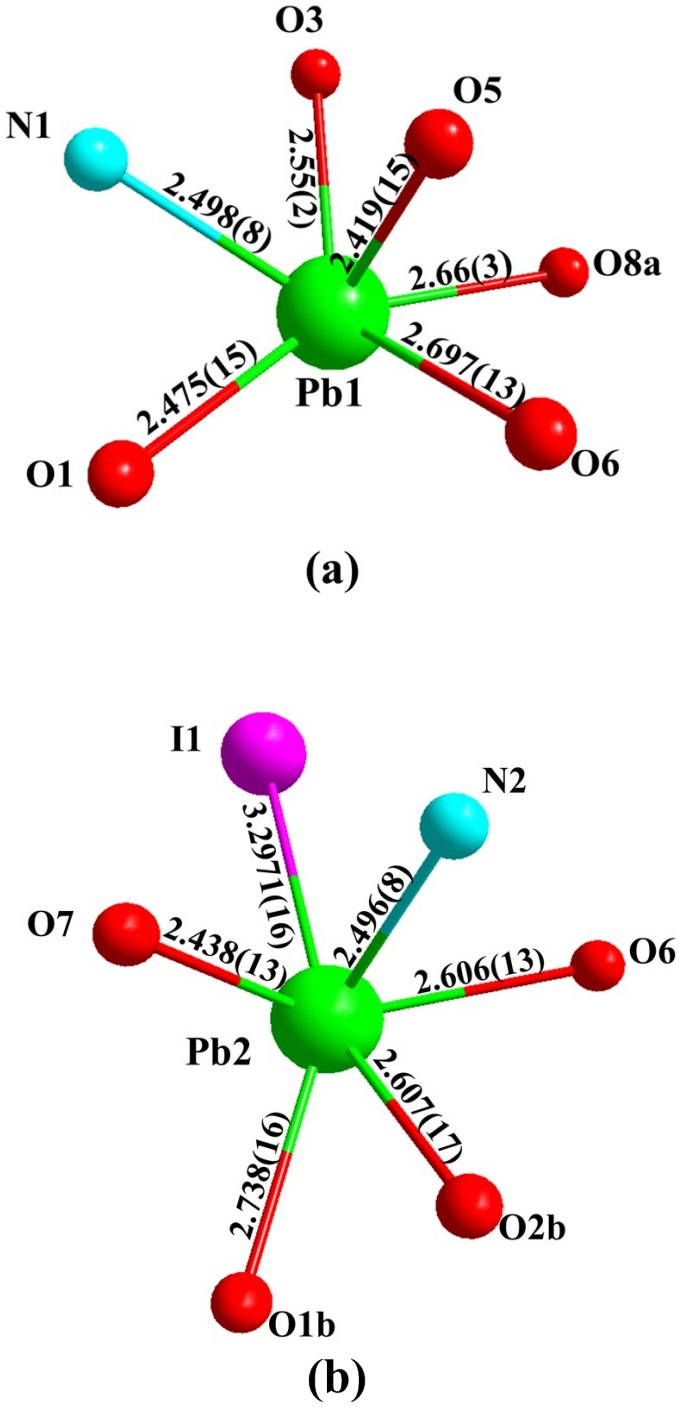


Figure S9. The coordination environments of (a) Pb1(II) and (b) Pb2(II) atoms. Symmetry codes: a 1/4 - x + 1, 3/4 - y, 1/4 + z; b 1/4 + x, 1/4 - y, 3/4 - z.

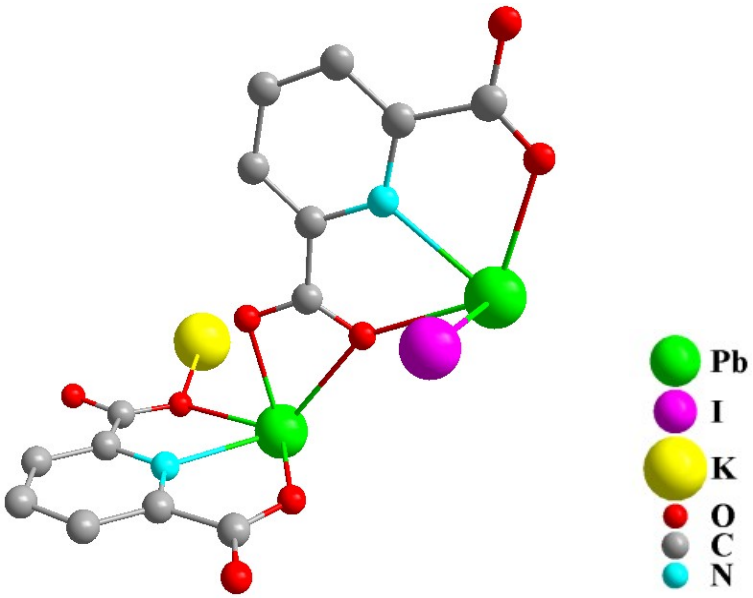


Figure S10. A ball-stick view of the structural unit of $KPb_2(C_7H_3NO_4)_2I$.

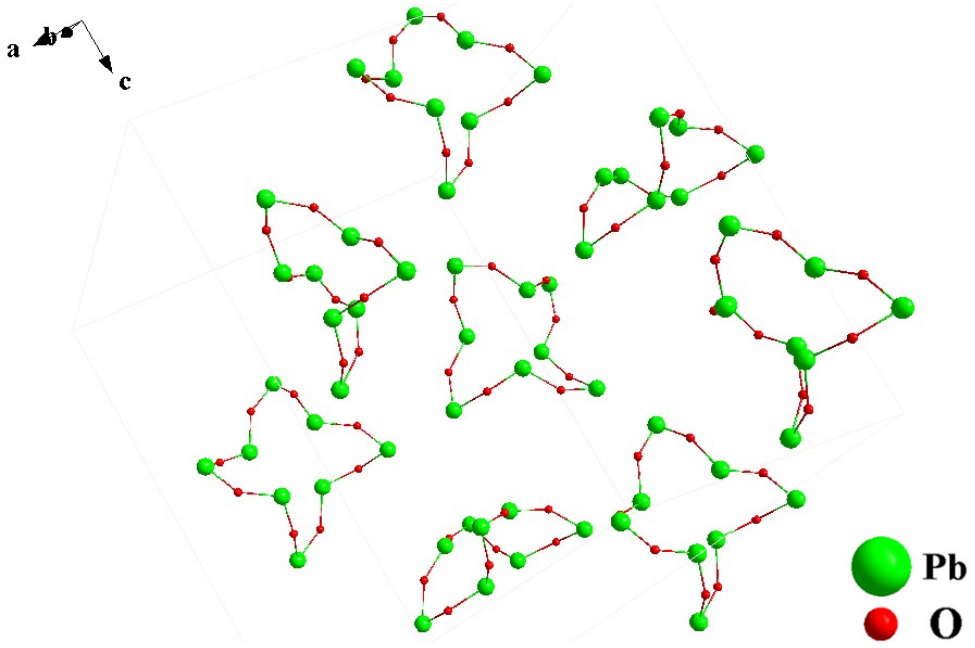


Figure S11. Twisted $[Pb_8O_8]$ 16-atom rings.

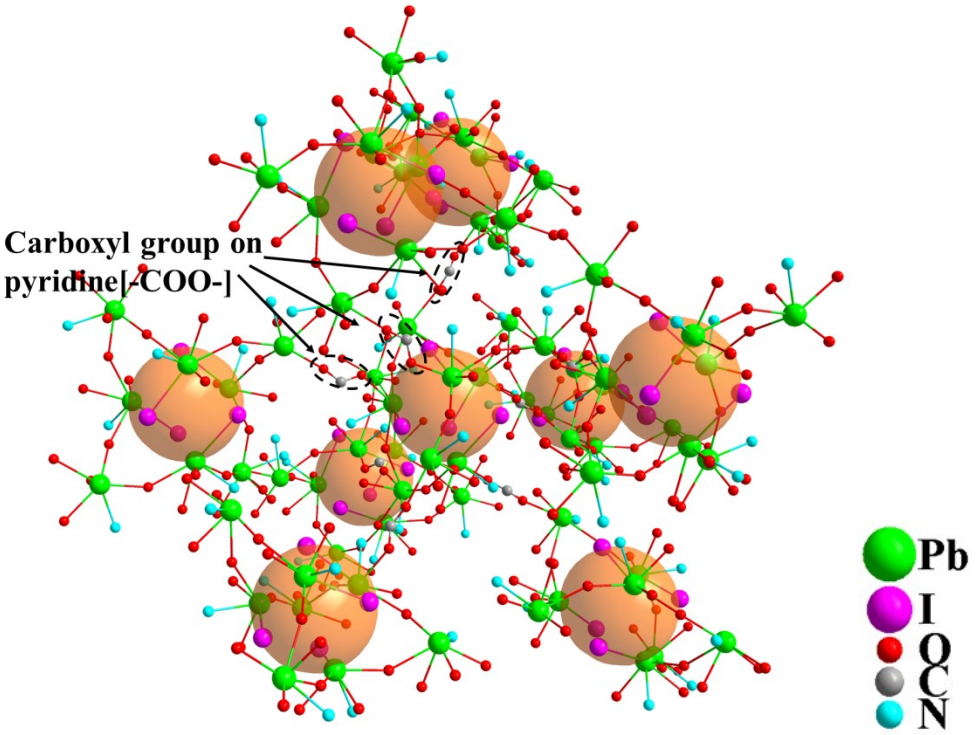


Figure S12. The NCS 3D framework. The large translucent orange sphere is the pseudoatom in the center of the 16-atom ring.

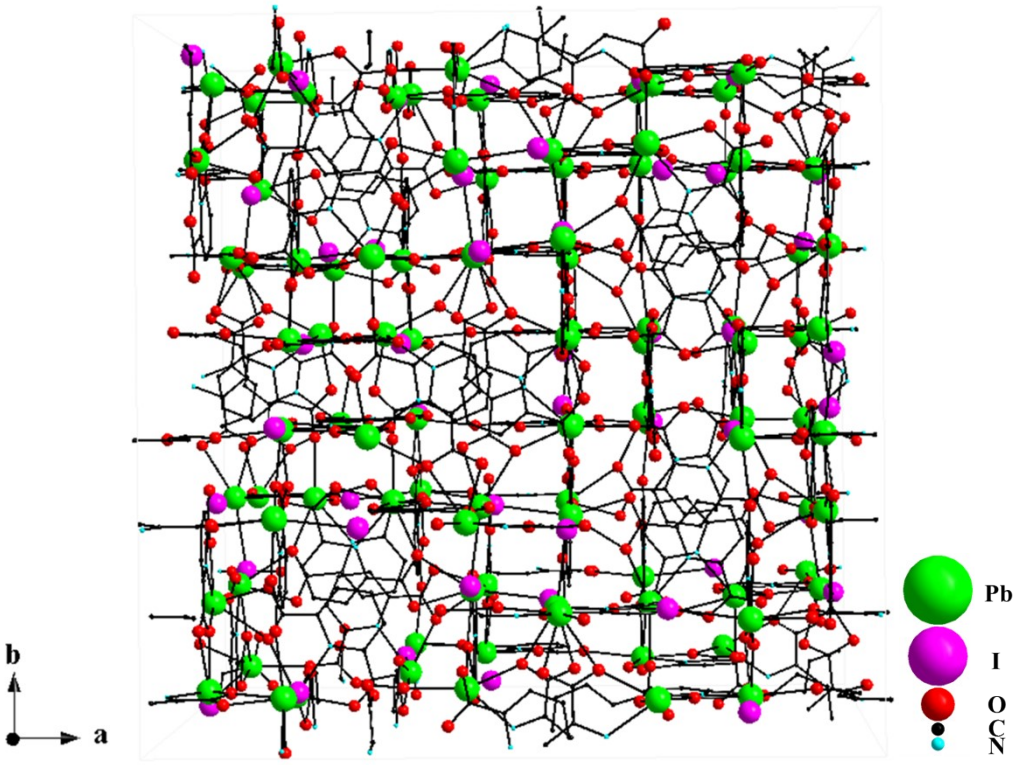


Figure S13. The 3D NCS cubic framework of $\mathbf{KPb_2(C_7H_3NO_4)_2I}$. Unrelated atoms are omitted for clarity.

3. References

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