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Tables and Figures

Table S1. Crystal data and structure refinements for $K_2[PbI_2(HCOO)_2]$.

Empirical formula	$K_2[PbI_2(HCOO)_2]$	$Rb_2[PbI_2(HCOO)_2]$
Formula weight	629.23	721.97
Temperature(K)	293.15	293.15
Crystal color	Light yellow	Colorless
Wavelength(Å)	1.3405	1.3405
Crystal system	Orthorhombic	Orthorhombic
Space group	*Amm*2	*Amm*2
a/Å	5.80240(10)	6.06620(10)
b/Å	6.7740(2)	6.79460(10)
c/Å	13.6260(4)	13.7817(3)
Volume / Å^3	535.58(2)	568.046(18)
Z, ρ_{calcd} / g·cm^{-3}	2, 3.902	2, 4.221
μ / mm^{-1}	56.272	55.500
F (000)	544	616
Data / restraints / parameters	473/1/37	571/1/37
2θ range for data collection/°	11.292 to 104.072	11.164 to 103.856
Limiting indices	$-6 \le h \le 6$, $-7 \le k \le 7$, $-15 \le l \le 16$	$-7 \le h \le 7$, $-7 \le k \le 7$, $-16 \le l \le 16$
Reflections collected / unique	2119/ 473 [R_{int} = 0.0373]	2207/571 [Rint = 0.0369]
Completeness	100%	100%
Goodness-of-fit on F^2	1.088	1.128
R_1, wR_2 ($I > 2\sigma$) [a]	R_1 = 0.0193, wR_2 = 0.0465	R_1 = 0.0185, wR_2 = 0.0421
R_1, wR_2 (all data)	R_1 = 0.0193, wR_2 = 0.0465	R_1 = 0.0186, wR_2 = 0.0421
Largest diff, peak and hole/ e·Å^{-3}	1.11 and -0.67	0.62 and -0.41
Flack parameter	0.03(2)	0.018(11)

[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 and equivalent isotropic displacement parameters (Å^2) of $K_2[PbI_2(HCOO)_2]$.

Atomic parameters

Atom	***Wyck.***	***x***	***y***	***z***	U_{eq}[a]	**BVS**[b]
Pb1	2b	0.5	0.5	0.56422(2)	0.0308(3)	1.59
K1	2a	0	0.5	0.3166(4)	0.0364(10)	0.97
K2	2a	0	0	0.4962(6)	0.0406(13)	1.29
I1	2a	0	0.5	0.68219(14)	0.0452(7)	-0.68
I2	2b	0.5	0	0.65397(10)	0.032(4)	-0.94
O1	8f	1	0.3093(12)	0.2818(10)	0.0375(15)	-2.23
C1	4e	0.5	0.2392(18)	0.3928(9)	0.031(3)	

Anisotropic displacement parameters (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	24.1(4)	38.9(5)	29.5(6)	0	0	0
K1	25(2)	44(3)	40(2)	0	0	0
K2	26(2)	35(2)	61(4)	0	0	0
I1	24.0(8)	51.6(10)	60.1(17)	0	0	0
I2	29.9(7)	35.6(8)	30.4(10)	0	0	0
O1	28(3)	43(4)	42(4)	6(4)	-2(3)	0(3)
C1	40(8)	22(7)	31(9)	3(5)	0	0

Table S3. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of $Rb_2[PbI_2(HCOO)_2]$.

Atomic parameters						
Atom	***Wyck.***	***x***	***y***	***z***	U_{eq}[a]	**BVS**[b]
Pb1	2b	0.5	0.5	0.42812(3)	0.0302(3)	1.56
Rb1	2a	1	1	0.48777(18)	0.0366(5)	1.62
Rb2	2a	1	0.5	0.67764(16)	0.0346(5)	1.55
I1	2b	1.5	1	0.33536(8)	0.0305(3)	-1.51
I2	2a	0	0.5	0.32236(12)	0.0429(4)	-0.74
O1	8f	0.6816(11)	0.7179(9)	0.5605(6)	0.0386(15)	-2.48
C1	4e	0.5	0.7605(19)	0.5969(9)	0.033(4)	

Anisotropic displacement parameters (Å^2)						
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	25.3(4)	37.5(5)	27.9(5)	0	0	0
Rb1	24.1(10)	35.7(11)	49.9(14)	0	0	0
Rb2	23.9(10)	45(11)	34.7(10)	0	0	0
I1	24.2(7)	39.2(8)	28(7)	0	0	0
I2	25.8(8)	40(9)	62.8(11)	0	0	0
O1	25(3)	46(4)	44(4)	7(4)	-3(4)	-2(3)
C1	48(10)	18(8)	34(7)	6(5)	0	0

Table S4. Selected bond length (**Å)** and angles (deg.) for $K_2[PbI_2(HCOO)_2]$.

Pb1-I1	3.3168(9)	Pb1-O1^2	2.605(8)
Pb1-I1^1	3.3168(9)	Pb1-O1^3	2.605(8)
Pb1-O1	2.605(8)	Pb1-O1^4	2.605(8)
I1-Pb1-I1^1	122.02(6)	I1^1-Pb1-O1^4	135.52(15)
I1-Pb1-O1	88.29(16)	O1-Pb1-O1^2	90.3(3)
I1-Pb1-O1^2	88.29(16)	O1-Pb1-O1^3	50.3(3)
I1-Pb1-O1^3	135.52(15)	O1-Pb1-O1^4	69.1(3)
I1-Pb1-O1^4	88.29(16)	O1^2-Pb1-O1^3	69.1(3)
I1^1-Pb1-O1	135.52(15)	O1^2-Pb1-O1^4	50.3(3)
I1^1-Pb1-O1^2	135.52(15)	O1^3-Pb1-O1^4	90.3(3)
I1^1-Pb1-O1^3	88.29(16)		

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

Table S5. Selected bond length (**Å)** and angles (deg.) for $Rb_2[PbI_2(HCOO)_2]$.

Pb1-I2	3.3651(8)	Pb1-O1^2	2.595(7)
Pb1-I2^1	3.3652(8)	Pb1-O1^3	2.595(7)
Pb1-O1	2.595(7)	Pb1-O1^4	2.595(7)
I2-Pb1-I2^1	128.67(5)	I2^1-Pb1- O1^4	85.53(16)
I2-Pb1-O1	133.40(14)	O1-Pb1-O1^2	90.6(3)
I2-Pb1-O1^2	85.53(16)	O1-Pb1-O1^3	50.2(3)
I2-Pb1-O1^3	85.53(16)	O1-Pb1-O1^4	69.6(3)
I2-Pb1- O1^4	133.40(14)	O1^2-Pb1-O1^3	69.6(3)
I2^1-Pb1-O1	85.53(16)	O1^2-Pb1-O1^4	50.2(3)
I2^1-Pb1- O1^2	133.40(14)	O1^3-Pb1-O1^4	90.6(3)
I2^1-Pb1- O1^3	133.40(14)		

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

Table S6. EDS and EA for $K_2[PbI_2(HCOO)_2]$ and $Rb_2[PbI_2(HCOO)_2]$

	Pb	I	K	Rb	C	H
$K_2[PbI_2(HCOO)_2]$	31.53%	40.33%	14.82%	-	3.75%	0.39%
$K_2[PbI_2(HCOO)_2]$ (Calc.)	32.93%	40.34%	12.43%	-	3.81%	0.32%
$Rb_2[PbI_2(HCOO)_2]$	28.70%	35.15%	-	23.66%	3.38%	0.42%
$Rb_2[PbI_2(HCOO)_2]$ (Calc.)	29.88%	39.66%	-	22.75%	3.33%	0.28%

Table S7 SHG responses and decomposition temperature of formates.

Crystal Name	Space Group	SHG response	Decomposition Temperature (N_2 condition)	References
$Cd(HCOO)_2{\cdot}2CS(NH_2)_2$	$P2_12_12_1$	2 × KDP	*	**[1]**
N,N′-diphenylguanidinium formate	$P2_1cn$	1.8 × KDP	203 °C	**[2]**
L-threonine formate	$P4_1$	1.21 × KDP	*	**[3]**
L-valine formate	*	0.5 × urea	*	**[4]**
$LiHCOO{\cdot}H_2O$(LFM)	$Pbn2_1$	0.9 × KDP	70 °C	**[5]**
L-alanine formate	$P2_12_12_1$	0.75 × KDP	234 °C	**[6]**
$Li_{0.9}Na_{0.1}HCOO{\cdot}H_2O$	*mm2*	0.8 × LFM	*	**[7]**
$Sr(HCOO)_2{\cdot}2H_2O$	$P2_12_12_1$	0.48 × KDP	72 °C	**[8]**
L-serine formate	$P2_1$	0.44 × KDP	*	**[9]**
$Ba(HCOO)_2$	$P2_12_12_1$	d_{36} = 0.32 × d_{36}(KDP)	*	**[10]**
NaHCOO	*mm2*	0.2 × LFM	*	**[7]**
$Y(HCOO)_3{\cdot}2H_2O$	$P2_12_12_1$	0.1 × KDP	*	**[11]**
$NH_4[Cu(HCOO)_3]$	$P2_12_12_1$	0.08 × KDP	82 °C	**[12]**
$[NH_4][Cd(HCOO)_3]$	$Pna2_1$	16 × quarts	100 °C	**[13]**
$KCs_2Pb_2(HCOO)_2Cl_5$	*Amm*2	4.2 × KDP	185 °C	**[14]**
$KCs_2[Pb_2Br_5(HCOO)_2]$	*Amm*2	6.5 × KDP	165 °C	**[15]**
$Rb_2[PbI_2(HCOO)_2]$	*Amm*2	6.8 × KDP	230 °C	**This work**
$K_2[PbI_2(HCOO)_2]$	*Amm*2	8 × KDP	240 °C	**This work**

* is not mentioned in the original articles.

Table S8. The local dipole moment (μ) in Debye for $K_2[PbI_2(HCOO)_2]$ and $Rb_2[PbI_2(HCOO)_2]$.

	$K_2[PbI_2(HCOO)_2]$			$Rb_2[PbI_2(HCOO)_2]$		
	μ_x	μ_y	μ_z	μ_x	μ_y	μ_z
PbI_2O_4	0	0	18.54	0	0	-17.81
PbI_2O_4	0	0	18.54	0	0	-17.81
HCOO	0	0.91	-1.56	0	0.89	1.54
HCOO	0	0.91	-1.56	0	0.89	1.54
HCOO	0	-0.91	-1.56	0	-0.89	1.54
HCOO	0	-0.91	-1.56	0	-0.89	1.54
Total	0	0	30.84	0	0	-29.46

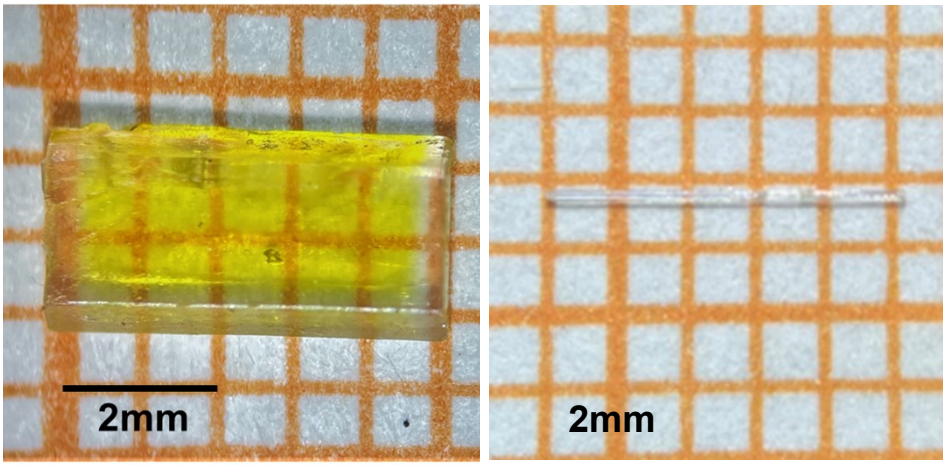


Figure S1. Photographs of the as-grown crystal without polishing for (a) $K_2[PbI_2(HCOO)_2]$ and (b) $Rb_2[PbI_2(HCOO)_2]$

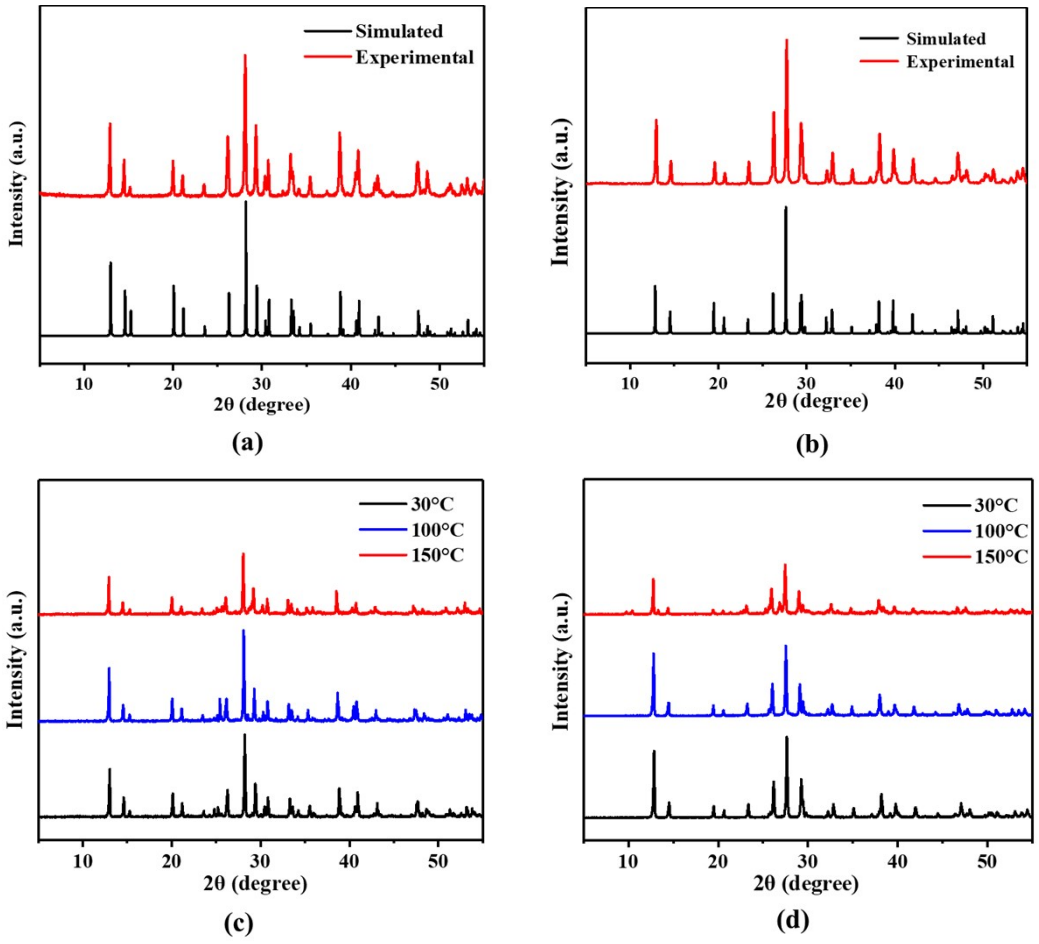
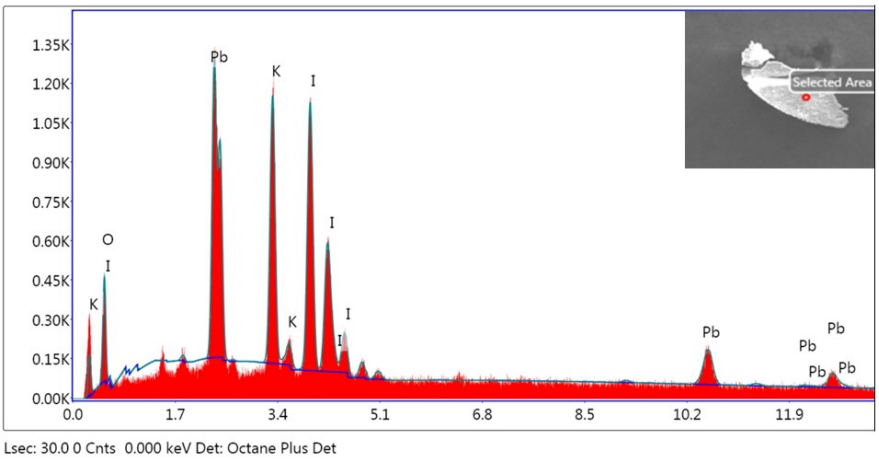
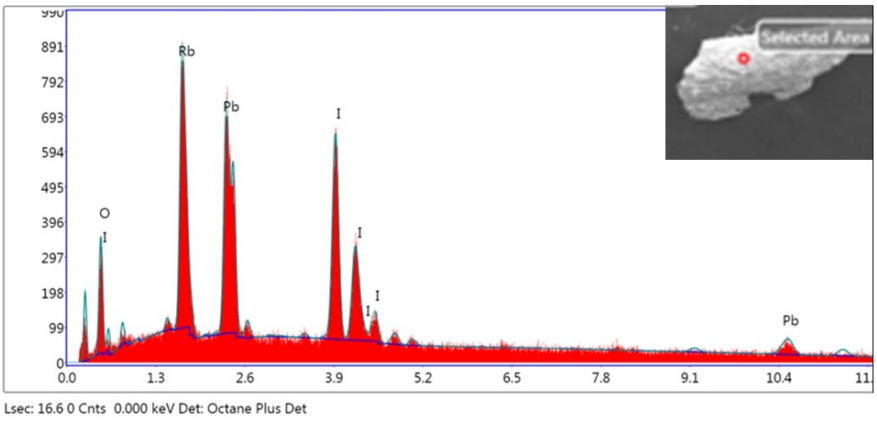


Figure S2. Experimental and simulated PXRD patterns of (a) $K_2[PbI_2(HCOO)_2]$ and (b) $Rb_2[PbI_2(HCOO)_2]$. Variable-temperature PXRD patterns of (c) $K_2[PbI_2(HCOO)_2]$ and (d) $Rb_2[PbI_2(HCOO)_2]$.



(a)



(b)

Figure S3. EDS spectra of (a) $K_2[PbI_2(HCOO)_2]$ and (b) $Rb_2[PbI_2(HCOO)_2]$.

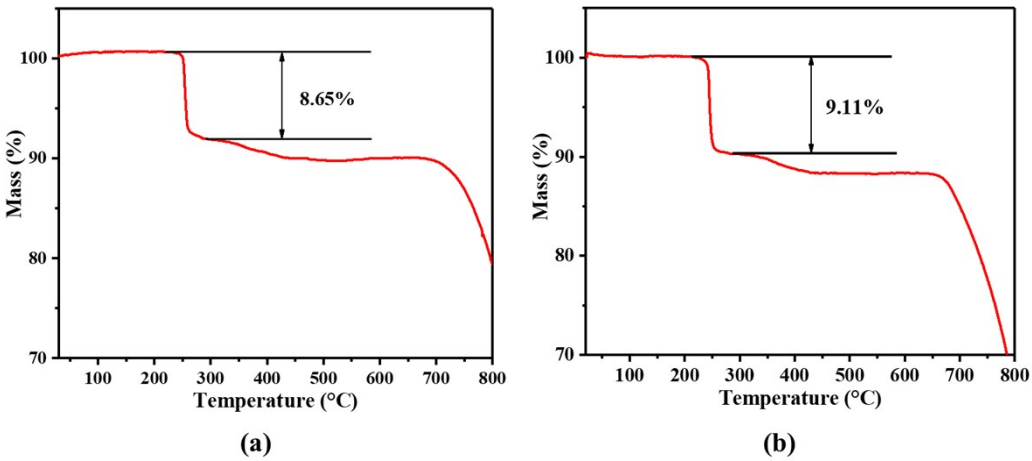


Figure S4. TG curves of (a) $K_2[PbI_2(HCOO)_2]$ and (b) $Rb_2[PbI_2(HCOO)_2]$.

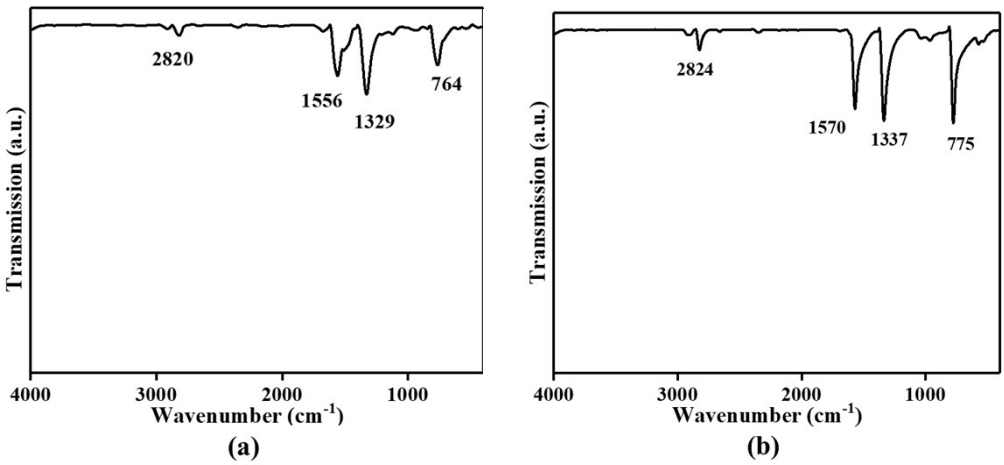


Figure S5. IR spectra of (a) $K_2[PbI_2(HCOO)_2]$ and (b) $Rb_2[PbI_2(HCOO)_2]$.

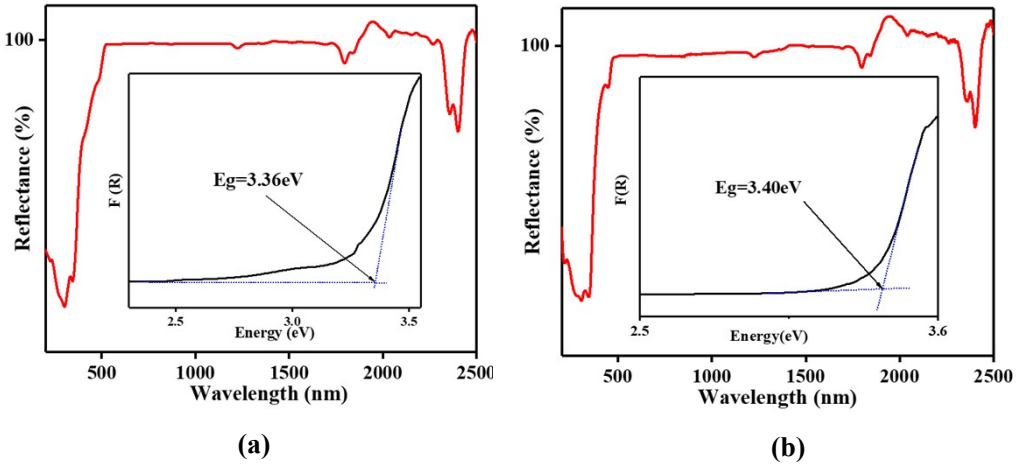


Figure S6. UV-Vis–NIR spectra of (a) $K_2[PbI_2(HCOO)_2]$ and (b) $Rb_2[PbI_2(HCOO)_2]$.

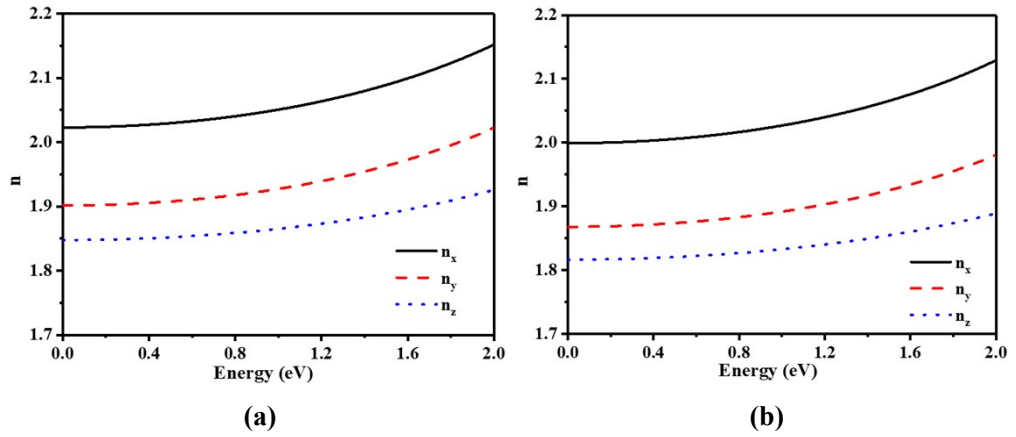


Figure S7. Optical refractive indices along principal axes of (a) $K_2[PbI_2(HCOO)_2]$ and (b) $Rb_2[PbI_2(HCOO)_2]$.

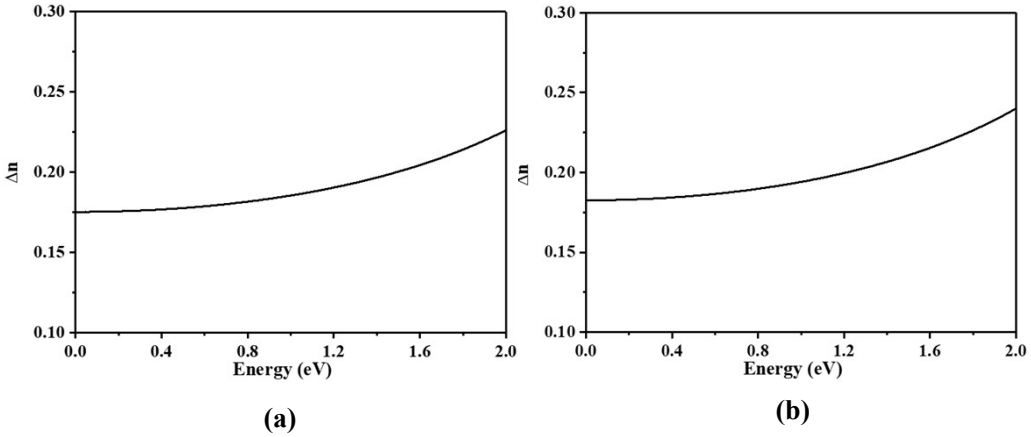


Figure S8. Optical birefringences *Δn* of (a) $K_2[PbI_2(HCOO)_2]$ and (b) $Rb_2[PbI_2(HCOO)_2]$ versus photon energy.

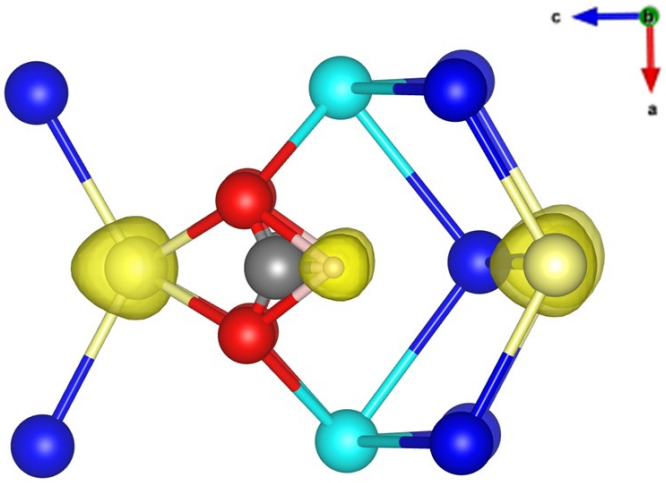


Figure S9. The ELF plot with an isovalue of 0.95. The beige lobes reflect the distribution of delocalized electrons. The Pb, K, I, C, H and O atoms are denoted by yellow, cyan, blue, gray, pink and red balls, respectively.

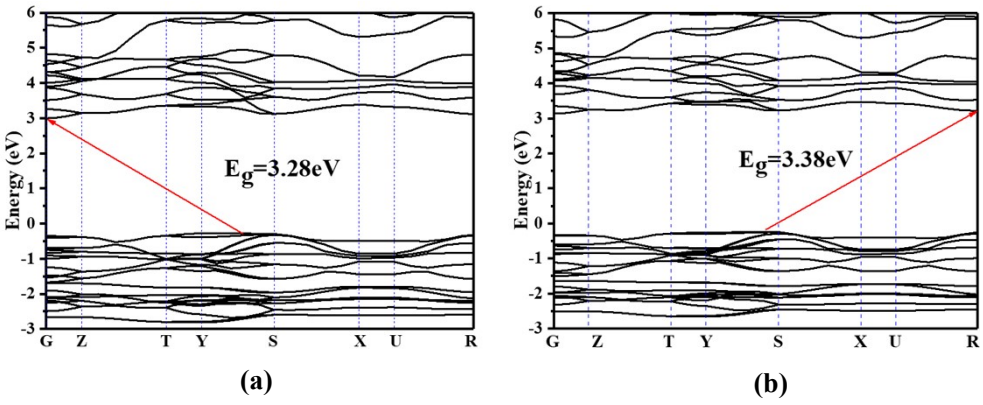


Figure S10. The calculated band structures of (a) $K_2[PbI_2(HCOO)_2]$ and (b) $Rb_2[PbI_2(HCOO)_2]$.

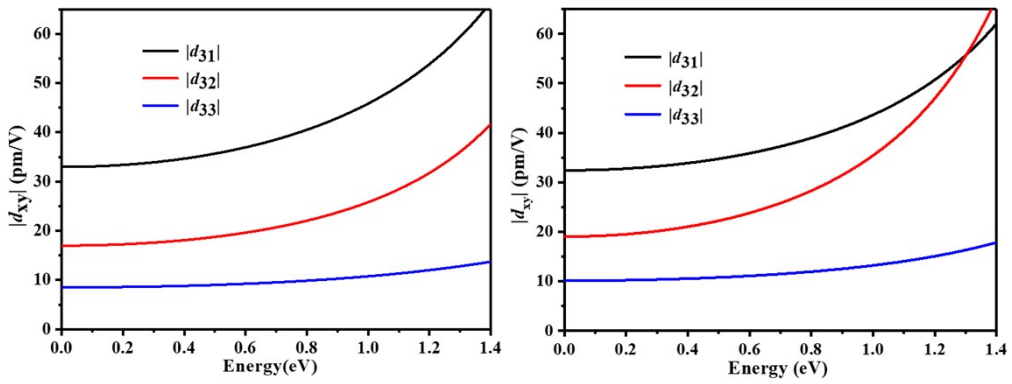


Figure S11. Frequency-dependent SHG coefficients of (a) $K_2[PbI_2(HCOO)_2]$ and (b) $Rb_2[PbI_2(HCOO)_2]$

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