Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Methylpiperazine Based 0D Chiral Hybrid Lead Halides for Second Harmonic Generation

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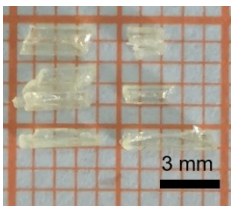

Figure S1. The optical image of (*S*-2-$C_5H_{14}N_2$)$_2PbI_6$ HOMH crystal.

Figure S2. Schematic diagram of crystal self-assembly.

Figure S3. An asymmetric unit structure of the (*rac*-2-$C_5H_{14}N_2$)$_2PbI_6$•$3H_2O$ HOMH crystal.

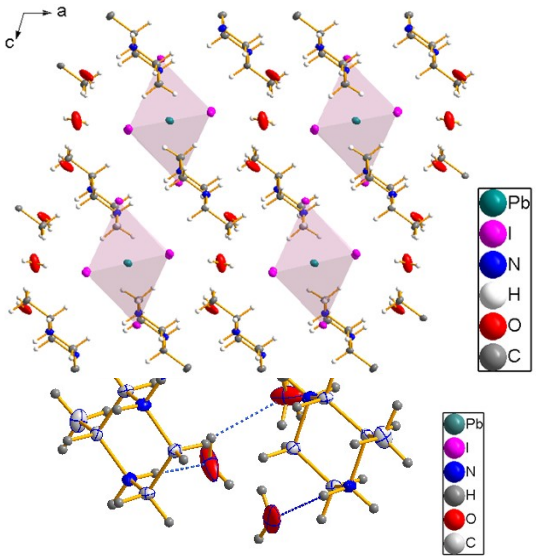

Figure S4. The packing framework of the (*rac*-2-$C_5H_{14}N_2$)$_2PbI_6$•$3H_2O$ HOMH crystal.

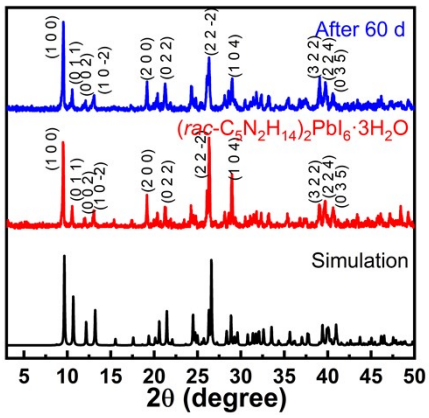

Figure S5. Powder XRD pattern of the (*rac*-2-$C_5H_{14}N_2)_2PbI_6$•$3H_2O$ HOMH crystal.

Figure S6. TG plot of (*S-/R*-2-$C_5H_{14}N_2)_2PbI_6$ and (*rac*-2-$C_5H_{14}N_2)_2PbI_6$•$3H_2O$ HOMHs.

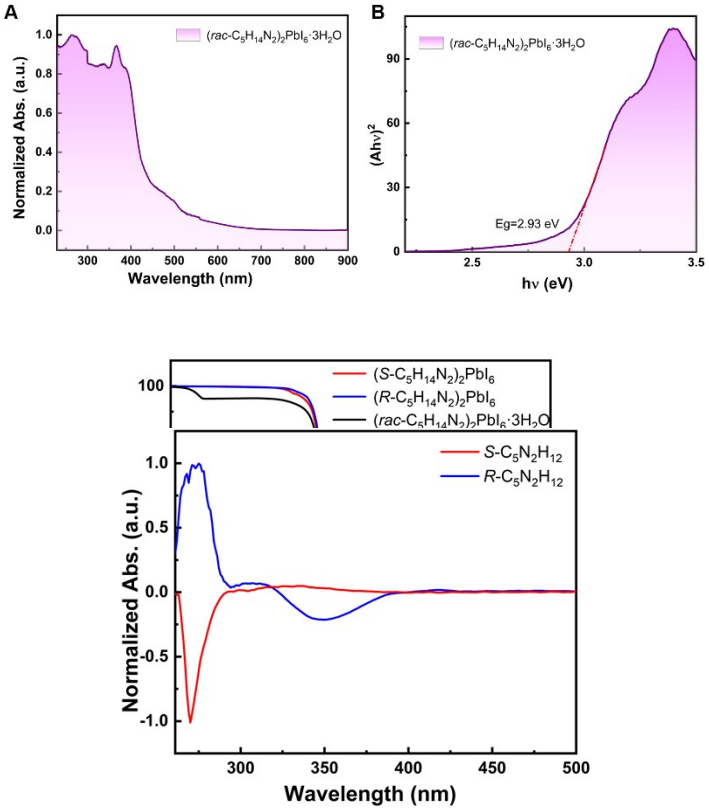

Figure S7. Linear optical properties of the (*rac*-2-$C_5H_{14}N_2)_2PbI_6$•$3H_2O$ HOMH crystal. A) Normalized UV-Vis DRS spectra. B) Optical band gap diagram calculated by Tauc method according to UV-Vis DRS spectra.

Figure S8. CD spectra of chiral organic amines (*S-/R*-$C_5N_2H_{12}$).

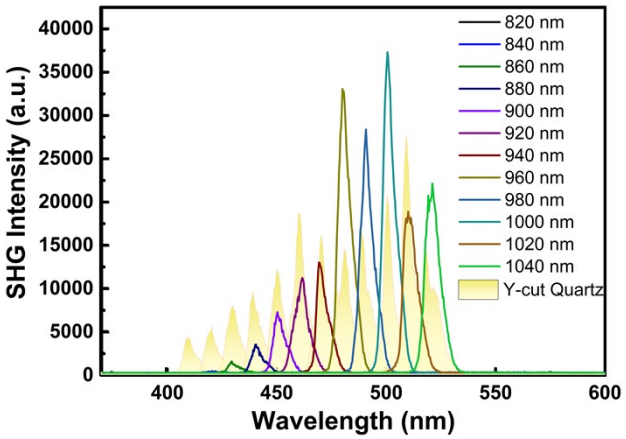

Figure S9. Comparison of the SHG intensity of Y-cut quartz and (*S*-2-$C_5H_{14}N_2$)$_2PbI_6$ single crystal excited at 820-1040 nm.

Table S1 Crystal Data and Structure Refinement for (*S/R*-2-$C_5H_{14}N_2$)$_2PbI_6$ and (*rac*-2-$C_5H_{14}N_2$)$_2PbI_6$•$3H_2O$ HOMHs.

Compound	(*S*-2-$C_5H_{14}N_2$)$_2PbI_6$	(*R*-2-$C_5H_{14}N_2$)$_2PbI_6$	(*rac*-2-$C_5H_{14}N_2$)$_2PbI_6$•$3H_2O$
Formula weight	584.48	586.48	611.49
Refinement method		Full-matrix least-squares on F^2	
Temperature		150 K	
Wavelength		0.71073 Å	
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*$P2_12_12$*	*$P2_12_12$*	*P2/c*
Unit cell dimensions	a = 14.6367(3)	a = 14.6421(5)	a = 9.5613(2)
	b = 10.2416(3)	b = 10.2354(3)	b = 10.0810(2)
	c = 8.7513(2)	c = 8.7575(2)	c = 15.1805(3)
Volume (Å^3)	1311.85(6)	1112.47(7)	1403.53(5)
Z	2	2	4
ρcalc (g/cm^3)	2.959	2.968	2.894
μ (mm^{-1})	13.489	13.485	12.620
F (000)	1028.0	1032.0	1082.0
2θ range	7.258 to 61.936	7.964 to 61.784	7.138 to 55
Index ranges	-20 ≤ h ≤ 20,	-19 ≤ h ≤ 20,	-12 ≤ h ≤ 12,
	-13 ≤ k ≤ 14,	-14 ≤ k ≤ 14,	-13 ≤ k ≤ 13,
	-12 ≤ l ≤ 12	-10 ≤ l ≤ 12	-19 ≤ l ≤ 19
Refl. collected	13688	13270	30754
Independent refl.	3625 [Rint = 0.0445]	3742 [Rint = 0.0538]	3213 [Rint = 0.0533]
Data/restr. / param.	3625/0/97	3742/0/97	3213/0/117
Goodness-of-fit on F^2	0.992	1.077	1.118
Final R indexes	R1 = 0.0220,	R1 = 0.0280,	R1 = 0.0189,
Final R indexes	R1 = 0.0232,	R1 = 0.0298,	R1 = 0.0199,
Largest diff. peak / hole (e Å^{-3})	2.10 / -1.76	1.12 / -1.75	0.66 / -1.71
Flack parameter	-0.004(3)	0.003(4)	-

Table S2 Crystal Bond Lengths and Angles of (*S*-2-$C_5H_{14}N_2)_2PbI_6$

Bond lengths (Å)			
Pb(1)-I(2)	3.2433(4)	N(1)-C(4)	1.495(7)
Pb(1)-I(2)^1	3.2433(4)	C(1)-C(2)	1.529(9)
Pb(1)-I(1)^1	3.1906(4)	C(1)-C(5)	1.505(9)
Pb(1)-I(1)	3.1906(4)	N(2)-C(2)	1.476(9)
Pb(1)-I(3)	3.2490(4)	N(2)-C(3)	1.486(9)
Pb(1)-I(3)^1	3.2490(4)	C(4)-C(3)	1.506(9)
N(1)-C(1)	1.507(8)		
Angle (degree)			
I(2)-Pb(1)- I(2)^1	97.270(16)	I(1)^1-Pb(1)- I(3)^1	91.685(11)
I(2) - Pb(1)- I(3)	81.829(11)	I(1)^1-Pb(1)- I(3)	100.311(11)
I(2)^1-Pb(1)- I(3)	87.790(11)	I(3)^1-Pb(1)- I(3)	164.283(18)
I(2)^1-Pb(1)- I(3)^1	81.828(11)	C(4)-N(1)-C(1)	113.1(5)
I(2) -Pb(1)- I(3)^1	87.789(11)	N(1)-C(1)-C(2)	108.4(5)
I(1)^1-Pb(1)- I(2)^1	91.051(10)	C(5)-C(1)-N(1)	109.0(5)
I(1)-Pb(1)- I(2)	91.052(10)	C(5)-C(1)-C(2)	112.3(6)
I(1)^1-Pb(1)- I(2)	171.498(12)	C(2)-N(2)-C(3)	112.3(5)
I(1) -Pb(1)- I(2)^1	171.498(12)	N(1)-C(4)-C(3)	109.6(5)
I(1)-Pb(1)- I(1)^1	80.690(16)	N(2)-C(2)-C(1)	111.3(5)
I(1)-Pb(1)- I(1)1	100.311(11)	N(2)-C(3)-C(4)	110.2(5)
I(1)-Pb(1)- I(3)	91.686(10)		

Table S3 Crystal Bond Lengths and Angles of (*R*-2-$C_5H_{14}N_2)_2PbI_6$

Bond lengths (Å)			
Pb(1)-I(1)	3.2429(6)	N(1)-C(4)	1.491(10)
Pb(1)-I(1)^1	3.2429(6)	C(1)-C(2)	1.531(11)
Pb(1)-I(3)^1	3.1923(6)	C(1)-C(5)	1.504(13)
Pb(1)-I(3)	3.1923(6)	C(4)-C(3)	1.514(11)
Pb(1)-I(2)	3.2506(6)	N(2)-C(2)	1.482(12)
Pb(1)-I(2)^1	3.2505(6)	N(2)-C(3)	1.479(11)
N(1)-C(1)	1.513(10)		
Angle (degree)			
I(1)-Pb(1)-I(1)^1	97.19(2)	I(3)^1-Pb(1)-I(2)	100.332(14)
I(1)-Pb(1)-I(2)	81.814(14)	I(3)^1-Pb(1)-I(2)^1	91.675(14)
I(1)^1-Pb(1)- I(2)	87.791(15)	I(2)^1-Pb(1)-I(2)	164.28 (2)
I(1)^1-Pb(1)-I(2)^1	81.814(14)	C(4)-N(1)-C(1)	112.4(7)
I(1)-Pb(1)-I(2)^1	87.791(15)	N(1)-C(1)-C(2)	107.9(7)
I(3)-Pb(1)-I(1)	91.114(13)	C(5)-C(1)-N(1)	108.6(7)
I(3)-Pb(1)-I(1)^1	171.512(15)	C(5)-C(1)-C(2)	111.5(8)
I(3)^1-Pb(1)-I(1)	171.512(15)	N(1)-C(4)-C(3)	110.1(7)
I(3)^1-Pb(1)-I(1)^1	91.114 (13)	C(3)-N(2)-C(2)	112.9(7)
I(3)-Pb(1)-I(3)^1	80.64(2)	N(2)-C(2)-C(1)	111.0(7)
I(3)-Pb(1)-I(2)^1	100.331(14)	N(2)-C(3)-C(4)	109.5(7)
I(3)-Pb(1)-I(2)	91.676(14)		

Table S4 Crystal Bond Lengths and Angles of (*rac*-2-$C_5H_{14}N_2$)$_2$$PbI_6$•3$H_2O$

Bond lengths (Å)			
Pb(1)-I(1)^1	3.3086(2)	N(2)-C(2)	1.494(4)
Pb(1)-I(1)	3.3086(2)	N(1)-C(1)	1.505(4)
Pb(1)-I(2)	3.2121(2)	N(1)-C(4)	1.493(4)
Pb(1)-I(2)^1	3.2121(2)	C(3)-C(4)	1.517(4)
Pb(1)-I(3)	3.1699(2)	C(1)-C(2)	1.513(4)
Pb(1)-I(3)^1	3.1699(2)	C(1)-C(5)	1.523(5)
N(2)-C(3)	1.494(4)		
Angle (degree)			
I(1)-Pb(1)-I(1)^1	80.102(8)	I(3)-Pb(1)-I(2)^1	96.641(6)
I(2)^1- Pb(1)-I(1)	85.059(6)	I(3)^1-Pb(1)-I(2)^1	89.506(6)
I(2)-Pb(1)-I(1)^1	85.058(6)	I(3)^1-Pb(1)-I(3)	88.664(9)
I(2)-Pb(1)-I(1)	88.372(6)	C(3)-N(2)-C(2)	111.8(2)
I(2)^1-Pb(1)-I(1)^1	88.372(6)	C(4)-N(1)-C(1)	111.2(2)
I(2)-Pb(1)-I(2)^1	171.418(9)	N(2)-C(3)-C(4)	110.6(3)
I(3)-Pb(1)-I(1)^1	95.642(5)	N(1)-C(1)-C(2)	109.1(3)
I(3)-Pb(1)-I(1)	175.393(6)	N(1)-C(1)-C(5)	109.6(3)
I(3)^1-Pb(1)-I(1)^1	175.393(6)	C(2)-C(1)-C(5)	111.6(3)
I(3)^1-Pb(1)-I(1)	95.642(5)	N(1)-C(3)-C(4)	111.0(3)
I(3)^1-Pb(1)-I(2)	96.641(6)	N(2)-C(2)-C(1)	110.5(3)
I(3)-Pb(1)-I(2)	89.507(6)		