Supporting Information

Tetrameric Cluster Assembled One-Dimensional Hybrid Lead Halides with Broadband light Emission

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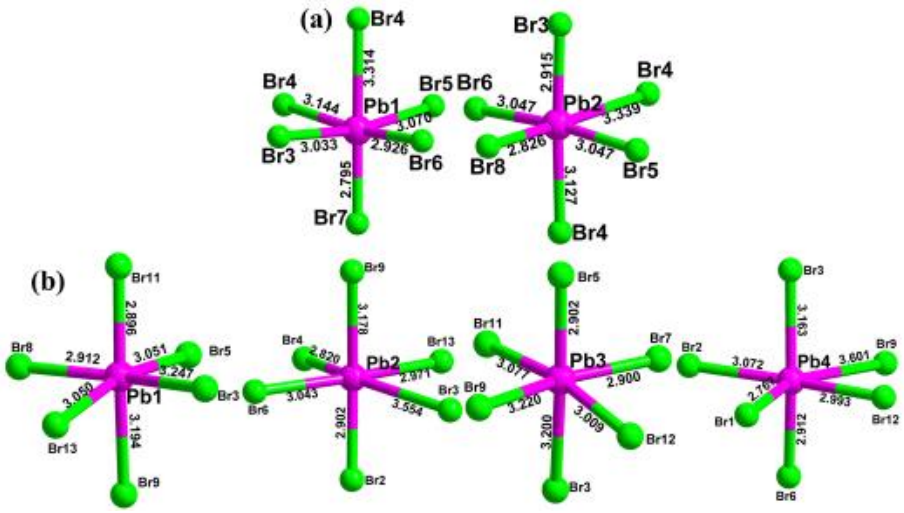

Fig. S1 Coordination environments of Pb^{2+} ions in compounds **1** (a) and **2** (b).

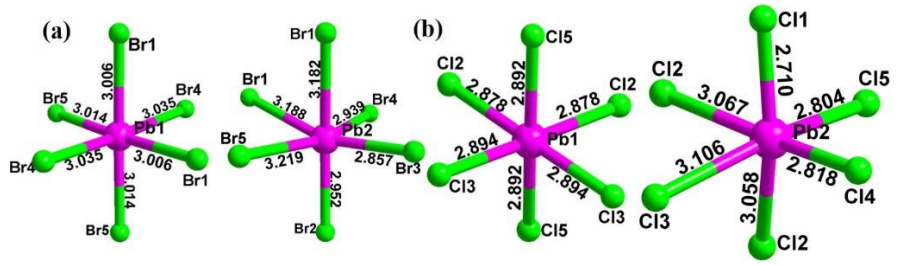

Fig. S2 Coordination environments of Pb^{2+} ions in compounds **3** (a) and **4** (b).

Fig. S3 The photo images of bulk crystal for compounds **1** (a), **2** (b), **3** (c) and **4** (d) under ambient light.

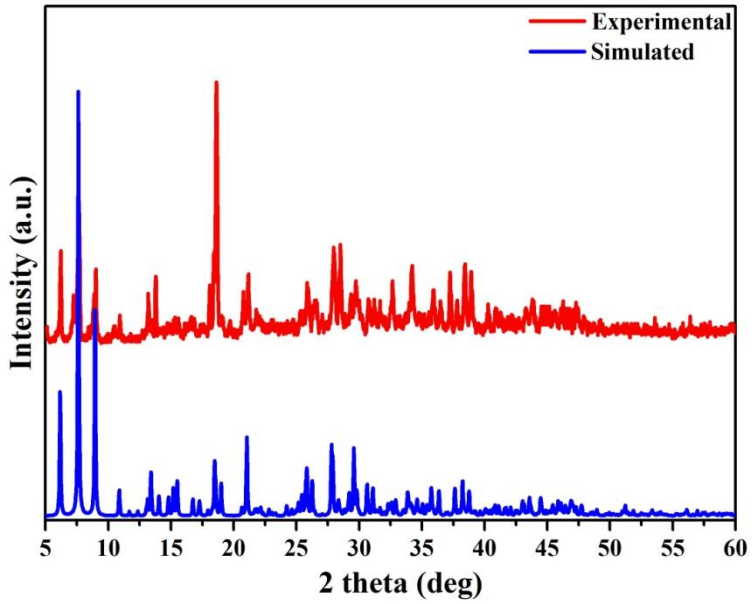

Fig. S4 The simulated and experimental XRD patterns of compound **2**.

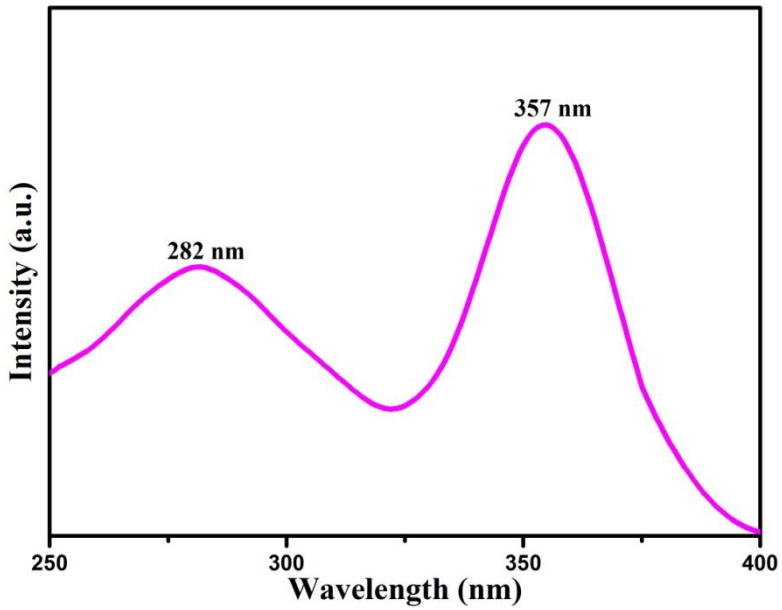

Fig. S5 The photoluminescence excitation spectrum of compound **2**.

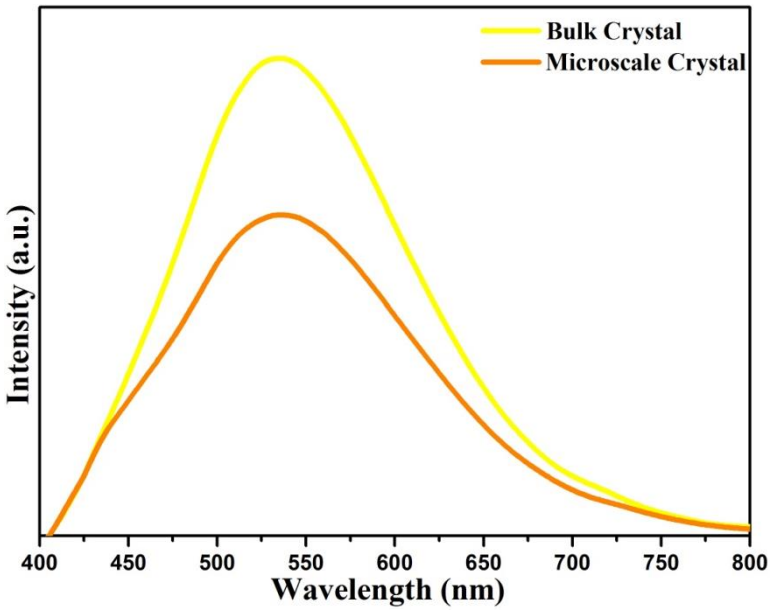

Fig. S6 Comparison of the photoluminescence emission spectra of bulk crystals and microscale crystals of compound **2**.

Table S1 Crystal Data and Structural Refinements of compounds **1 - 4**.

	1	**2**	**3**	**4**
chemical formula	$C_4N_2H_{16}OPb_2Br_6$	$C_9N_2H_{23}OPb_2Br_6$	$C_{14}N_4H_{40}Pb_3Br_{10}$	$C_{14}N_4H_{40}Pb_3Cl_{10}$
fw	1002.03	1069.13	1685.17	1240.60
Space group	$P2_1/n$	$P2_1$	$C2/c$	$C2/c$
a/Å	7.7317(13)	8.194(15)	14.597(4)	24.6238(17)
b/Å	11.617(2)	19.75(4)	12.063(3)	11.6554(8)
c/Å	20.846(4)	14.33(3)	21.211(7)	14.3516(10)
β/°	92.684(2)	92.072(17)	91.264(3)	124.349(3)
V(Å^3)	1870.3(6)	2317(7)	3734.1(18)	3400.6(4)
Z	4	4	4	4
D_{calcd} (g·cm^{-3})	3.559	3.064	2.998	2.423
Temp (K)	296(2)	296(2)	296(2)	296(2)
μ (mm^{-1})	30.782	24.855	24.206	15.614
F(000)	1744	1892	2992	2271
Reflections collected	22024	24734	21759	19969
Unique reflections	4422	8915	4613	3925
Reflections ($I>2\sigma(I)$)	3419	5686	3278	3321
GOF on F^2	1.016	0.952	1.041	1.060
R_1,wR_2 ($I > 2\sigma(I)$)[a]	0.0413/0.0929	0.0361/0.0535	0.0518/0.1211	0.0242/0.0551
R_1,wR_2 (all data)	0.0627/0.1015	0.0778/0.0621	0.0822/0.1349	0.0317/0.0575
$\Delta\rho_{max}$ (e/Å^3)	3.636	0.908	3.408	0.648
$\Delta\rho_{min}$ (e/Å^3)	-2.612	-0.799	-3.219	-1.591

Table S2 Bond lengths [Å] and angles [°] for compound **1**.

Pb(1)-Br(5)	2.7952(13)	Pb(2)-Br(6)	2.8259(12)
Pb(1)-Br(4)	2.9266(12)	Pb(2)-Br(1)	2.9152(11)
Pb(1)-Br(1)	3.0330(12)	Pb(2)-Br(4)#1	3.0473(13)
Pb(1)-Br(3)	3.0704(12)	Pb(2)-Br(3)#2	3.0478(12)
Pb(1)-Br(2)	3.1437(11)	Pb(2)-Br(2)#3	3.1271(11)
Br(5)-Pb(1)-Br(4)	93.89(4)	Br(6)-Pb(2)-Br(1)	91.52(3)
Br(5)-Pb(1)-Br(1)	94.87(4)	Br(6)-Pb(2)-Br(4)#1	87.81(4)
Br(4)-Pb(1)-Br(1)	90.25(3)	Br(1)-Pb(2)-Br(4)#1	93.35(3)
Br(5)-Pb(1)-Br(3)	94.40(4)	Br(6)-Pb(2)-Br(3)#2	90.38(3)
Br(4)-Pb(1)-Br(3)	92.49(4)	Br(1)-Pb(2)-Br(3)#2	91.75(3)
Br(1)-Pb(1)-Br(3)	170.13(3)	Br(4)#1-Pb(2)-Br(3)#2	174.63(3)
Br(5)-Pb(1)-Br(2)	94.11(3)	Br(6)-Pb(2)-Br(2)#3	90.14(3)
Br(4)-Pb(1)-Br(2)	171.48(3)	Br(1)-Pb(2)-Br(2)#3	177.56(3)
Br(1)-Pb(1)-Br(2)	86.14(3)	Br(4)#1-Pb(2)-Br(2)#3	88.50(3)
Br(3)-Pb(1)-Br(2)	89.83(3)	Br(3)#2-Pb(2)-Br(2)#3	86.45(3)

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

Table S3 Bond lengths [Å] and angles [°] for compound **2**.

Pb(1)-Br(3)	2.894(6)	Pb(3)-Br(10)	2.891(7)
Pb(1)-Br(9)	2.923(7)	Pb(3)-Br(12)	2.902(6)
Pb(1)-Br(1)	3.043(6)	Pb(3)-Br(2)	3.016(6)
Pb(1)-Br(12)	3.058(5)	Pb(3)-Br(3)#1	3.066(6)
Pb(1)-Br(8)#1	3.196(6)	Pb(3)-Br(5)#1	3.200(6)
Pb(2)-Br(4)	2.803(7)	Pb(3)-Br(8)#1	3.210(6)
Pb(2)-Br(6)	2.899(6)	Pb(4)-Br(7)	2.784(7)
Pb(2)-Br(1)	2.965(6)	Pb(4)-Br(11)	2.916(6)
Pb(2)-Br(11)#2	3.047(6)	Pb(4)-Br(2)	2.998(6)
Pb(2)-Br(8)	3.178(6)	Pb(4)-Br(6)	3.068(6)
Br(3)-Pb(1)-Br(9)	91.72(16)	Pb(4)-Br(5)	3.162(6)
Br(3)-Pb(1)-Br(1)	101.86(18)	Br(10)-Pb(3)-Br(12)	91.16(16)
Br(9)-Pb(1)-Br(1)	84.33(19)	Br(10)-Pb(3)-Br(2)	83.56(19)
Br(3)-Pb(1)-Br(12)	91.64(19)	Br(12)-Pb(3)-Br(2)	99.47(18)
Br(9)-Pb(1)-Br(12)	97.62(17)	Br(10)-Pb(3)-Br(3)#1	96.37(18)
Br(1)-Pb(1)-Br(12)	166.31(14)	Br(12)-Pb(3)-Br(3)#1	92.58(19)
Br(3)-Pb(1)-Br(8)#1	173.87(13)	Br(2)-Pb(3)-Br(3)#1	167.95(13)
Br(9)-Pb(1)-Br(8)#1	87.16(15)	Br(10)-Pb(3)-Br(5)#1	87.99(15)
Br(1)-Pb(1)-Br(8)#1	84.04(17)	Br(12)-Pb(3)-Br(5)#1	175.49(14)
Br(12)-Pb(1)-Br(8)#1	82.54(17)	Br(2)-Pb(3)-Br(5)#1	84.84(17)
Br(4)-Pb(2)-Br(6)	91.07(18)	Br(3)#1-Pb(3)-Br(5)#1	83.11(17)
Br(4)-Pb(2)-Br(1)	86.02(19)	Br(10)-Pb(3)-Br(8)#1	161.02(15)
Br(6)-Pb(2)-Br(1)	93.03(19)	Br(12)-Pb(3)-Br(8)#1	84.77(16)
Br(4)-Pb(2)-Br(11)#2	86.11(18)	Br(2)-Pb(3)-Br(8)#1	78.86(18)
Br(6)-Pb(2)-Br(11)#2	86.5(2)	Br(3)#1-Pb(3)-Br(8)#1	102.32(18)
Br(1)-Pb(2)-Br(11)#2	172.11(15)	Br(5)#1-Pb(3)-Br(8)#1	97.43(15)
Br(4)-Pb(2)-Br(8)	98.03(16)	Br(7)-Pb(4)-Br(11)	90.11(17)
Br(6)-Pb(2)-Br(8)	169.21(14)	Br(7)-Pb(4)-Br(2)	86.03(18)
Br(1)-Pb(2)-Br(8)	93.37(19)	Br(11)-Pb(4)-Br(2)	93.92(19)
Br(11)#2-Pb(2)-Br(8)	88.36(19)	Br(7)-Pb(4)-Br(6)	85.24(17)
Br(11)-Pb(4)-Br(5)	169.98(15)	Br(11)-Pb(4)-Br(6)	88.4(2)
Br(2)-Pb(4)-Br(5)	92.58(18)	Br(2)-Pb(4)-Br(6)	170.97(14)
Br(6)-Pb(4)-Br(5)	86.33(18)	Br(7)-Pb(4)-Br(5)	97.94(16)

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

Table S4 Bond lengths [Å] and angles [°] for compound **3**.

Pb(1)-Br(1)#1	3.0060(12)	Pb(2)-Br(3)	2.8570(13)
Pb(1)-Br(1)	3.0060(12)	Pb(2)-Br(4)	2.9388(13)
Pb(1)-Br(5)#1	3.0139(12)	Pb(2)-Br(2)	2.9518(13)
Pb(1)-Br(5)	3.0139(12)	Pb(2)-Br(1)#2	3.1825(13)
Pb(1)-Br(4)	3.0350(15)	Pb(2)-Br(1)	3.1878(15)
Pb(1)-Br(4)#1	3.0350(15)	Pb(2)-Br(5)#2	3.2189(13)
Br(1)#1-Pb(1)-Br(1)	90.12(5)	Br(3)-Pb(2)-Br(4)	91.58(4)
Br(1)#1-Pb(1)-Br(5)#1	87.39(4)	Br(3)-Pb(2)-Br(2)	90.94(4)
Br(1)-Pb(1)-Br(5)#1	177.30(3)	Br(4)-Pb(2)-Br(2)	93.95(5)
Br(1)#1-Pb(1)-Br(5)	177.30(3)	Br(3)-Pb(2)-Br(1)#2	83.97(4)
Br(1)-Pb(1)-Br(5)	87.39(4)	Br(4)-Pb(2)-Br(1)#2	93.30(4)
Br(5)#1-Pb(1)-Br(5)	95.12(5)	Br(2)-Pb(2)-Br(1)#2	171.25(3)
Br(1)#1-Pb(1)-Br(4)	90.76(4)	Br(3)-Pb(2)-Br(1)	161.94(3)
Br(1)-Pb(1)-Br(4)	83.79(3)	Br(4)-Pb(2)-Br(1)	82.26(3)
Br(5)#1-Pb(1)-Br(4)	97.28(3)	Br(2)-Pb(2)-Br(1)	106.36(4)
Br(5)-Pb(1)-Br(4)	87.93(4)	Br(1)#2-Pb(2)-Br(1)	79.48(3)
Br(1)#1-Pb(1)-Br(4)#1	83.79(3)	Br(3)-Pb(2)-Br(5)#2	101.40(4)
Br(1)-Pb(1)-Br(4)#1	90.76(4)	Br(4)-Pb(2)-Br(5)#2	165.13(3)
Br(5)#1-Pb(1)-Br(4)#1	87.93(4)	Br(2)-Pb(2)-Br(5)#2	93.06(4)
Br(5)-Pb(1)-Br(4)#1	97.28(3)	Br(1)#2-Pb(2)-Br(5)#2	81.03(3)
Br(4)-Pb(1)-Br(4)#1	172.30(6)	Br(1)-Pb(2)-Br(5)#2	83.19(3)

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

Table S5 Bond lengths [Å] and angles [°] for compound **4**.

Pb(1)-Cl(2)	2.8778(11)	Pb(2)-Cl(1)	2.7108(11)
Pb(1)-Cl(2)#1	2.8778(11)	Pb(2)-Cl(5)	2.8028(14)
Pb(1)-Cl(5)#2	2.8930(14)	Pb(2)-Cl(4)	2.8165(12)
Pb(1)-Cl(5)#3	2.8930(14)	Pb(2)-Cl(2)#3	3.0574(12)
Pb(1)-Cl(3)	2.8935(11)	Pb(2)-Cl(2)	3.0666(12)
Pb(1)-Cl(3)#1	2.8935(11)	Pb(2)-Cl(3)	3.1082(13)
Cl(2)-Pb(1)-Cl(2)#1	94.07(5)	Cl(1)-Pb(2)-Cl(5)	90.96(4)
Cl(2)-Pb(1)-Cl(5)#2	89.57(5)	Cl(1)-Pb(2)-Cl(4)	91.13(4)
Cl(2)#1-Pb(1)-Cl(5)#2	81.50(4)	Cl(5)-Pb(2)-Cl(4)	91.64(5)
Cl(2)-Pb(1)-Cl(5)#3	81.50(4)	Cl(1)-Pb(2)-Cl(2)#3	157.98(3)
Cl(2)#1-Pb(1)-Cl(5)#3	89.57(5)	Cl(5)-Pb(2)-Cl(2)#3	79.88(4)
Cl(5)#2-Pb(1)-Cl(5)#3	166.91(7)	Cl(4)-Pb(2)-Cl(2)#3	108.98(4)
Cl(2)-Pb(1)-Cl(3)	85.06(4)	Cl(1)-Pb(2)-Cl(2)	82.41(3)
Cl(2)#1-Pb(1)-Cl(3)	179.13(3)	Cl(5)-Pb(2)-Cl(2)	95.35(5)
Cl(5)#2-Pb(1)-Cl(3)	98.51(4)	Cl(4)-Pb(2)-Cl(2)	170.54(3)
Cl(5)#3-Pb(1)-Cl(3)	90.27(5)	Cl(2)#3-Pb(2)-Cl(2)	78.61(3)
Cl(2)-Pb(1)-Cl(3)#1	179.13(3)	Cl(1)-Pb(2)-Cl(3)	99.93(3)
Cl(2)#1-Pb(1)-Cl(3)#1	85.06(4)	Cl(5)-Pb(2)-Cl(3)	166.50(4)
Cl(5)#2-Pb(1)-Cl(3)#1	90.28(5)	Cl(4)-Pb(2)-Cl(3)	96.07(4)
Cl(5)#3-Pb(1)-Cl(3)#1	98.51(4)	Cl(2)#3-Pb(2)-Cl(3)	87.13(3)
Cl(3)-Pb(1)-Cl(3)#1	95.81(5)	Cl(2)-Pb(2)-Cl(3)	78.36(3)

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