Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Organic Cations Directed Hybrid Lead Halides of Zero-Dimensional to Two-Dimensional Structures with Tunable Photoluminescent Properties

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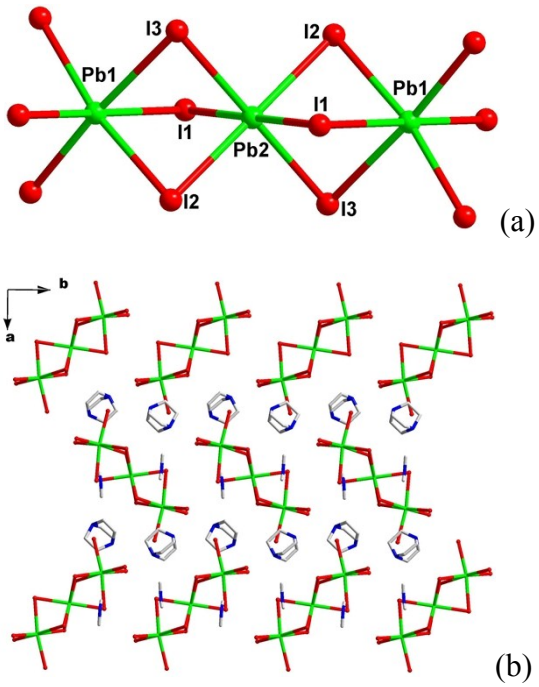

Fig. S1. Detailed view of the linear $[Pb_3I_{12}]^{6-}$ oligomer (a) and packing manner in [001] plane (b) in compound **1**.

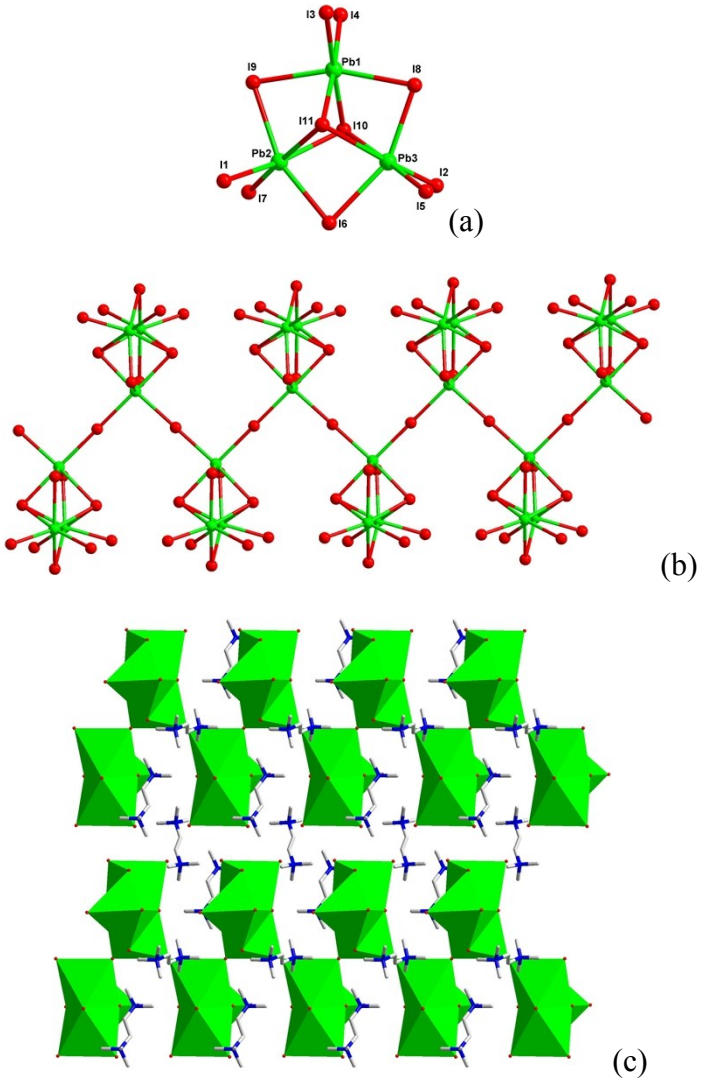

Fig. S2. Detailed view of the $[Pb_3I_{11}]$ trimer (a), 1D $[Pb_3I_{10}]^{4-}$ double chain (b) and 3D packing manner of 1D $[Pb_3I_{10}]^{4-}$ chain (c) in compound **2**. The green polyhedrons represent the 1D $[Pb_3I_{10}]^{4-}$ chain.

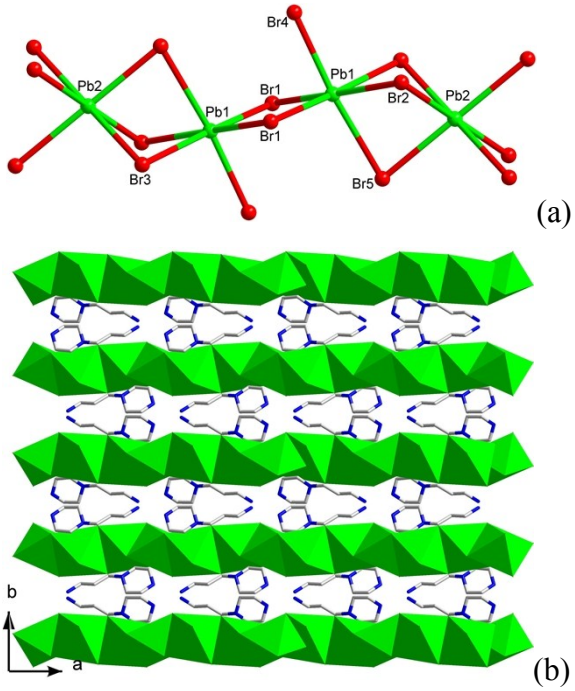

Fig. S3. The 1D $[Pb_3Br_{10}]^{4-}$ chain (a) and the 3D packing structure (b) in compound **3**.

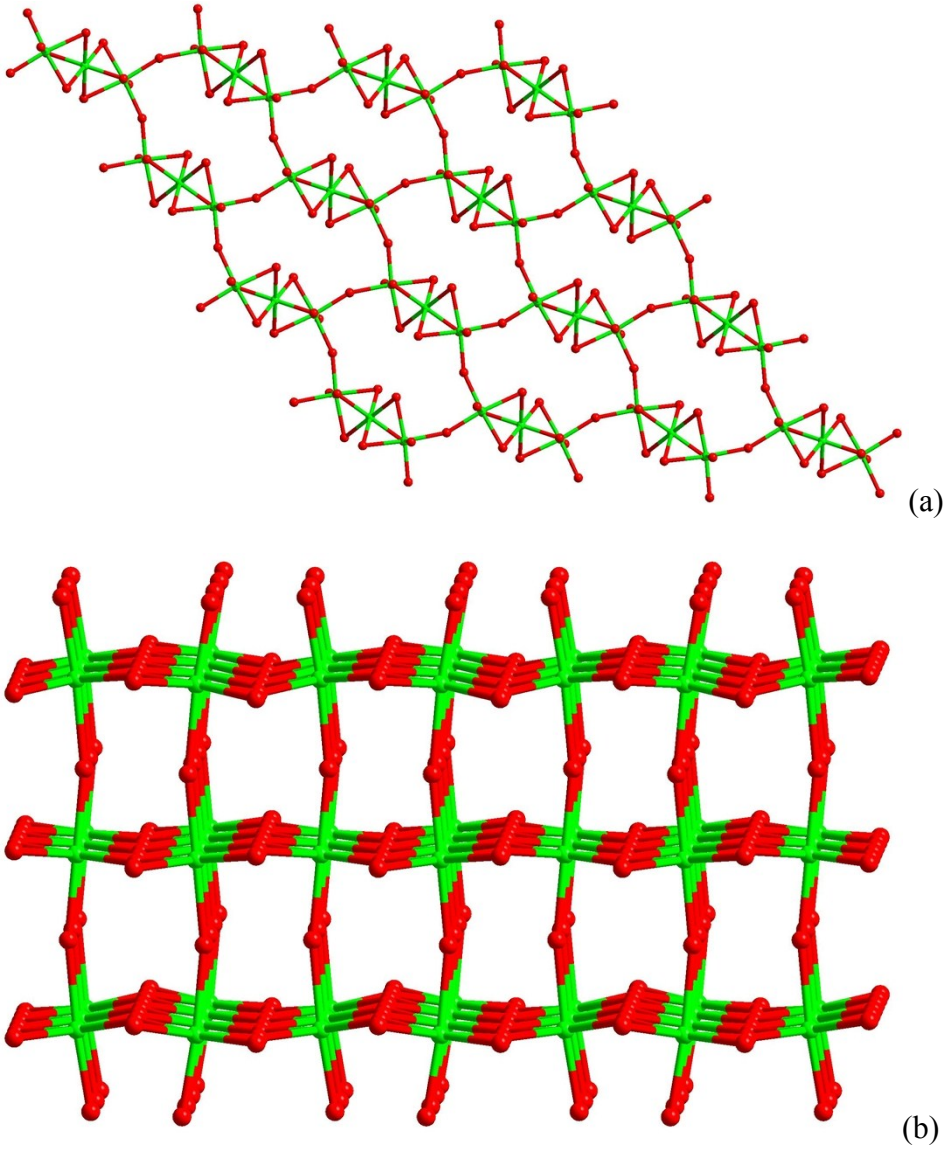

Fig. S4. The 2D $[Pb_3X_{10}]^{4-}$ layers composed of linear $[Pb_3X_{12}]$ trimers (a) and three-layered $[Pb_3X_{10}]^{4-}$ perovskite (b).

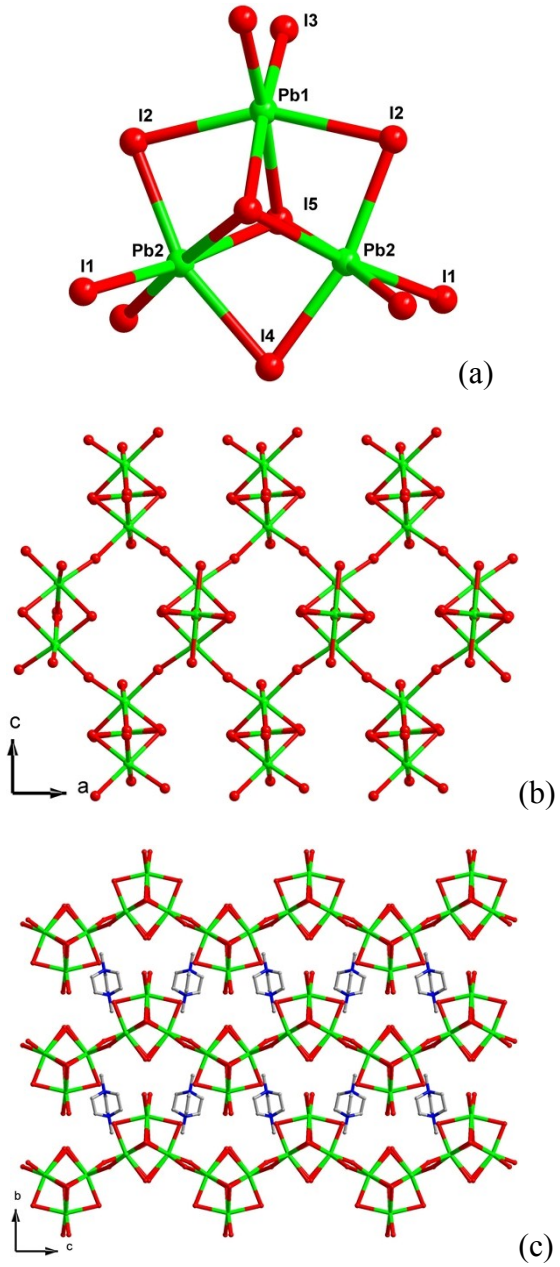

Fig. S5. Detailed view of $[Pb_3I_{11}]^{5-}$ trimer (a), the 2D corrugated $[Pb_3I_9]^{3-}$ layer (b), and the 3D packing structure of compound **4** (c).

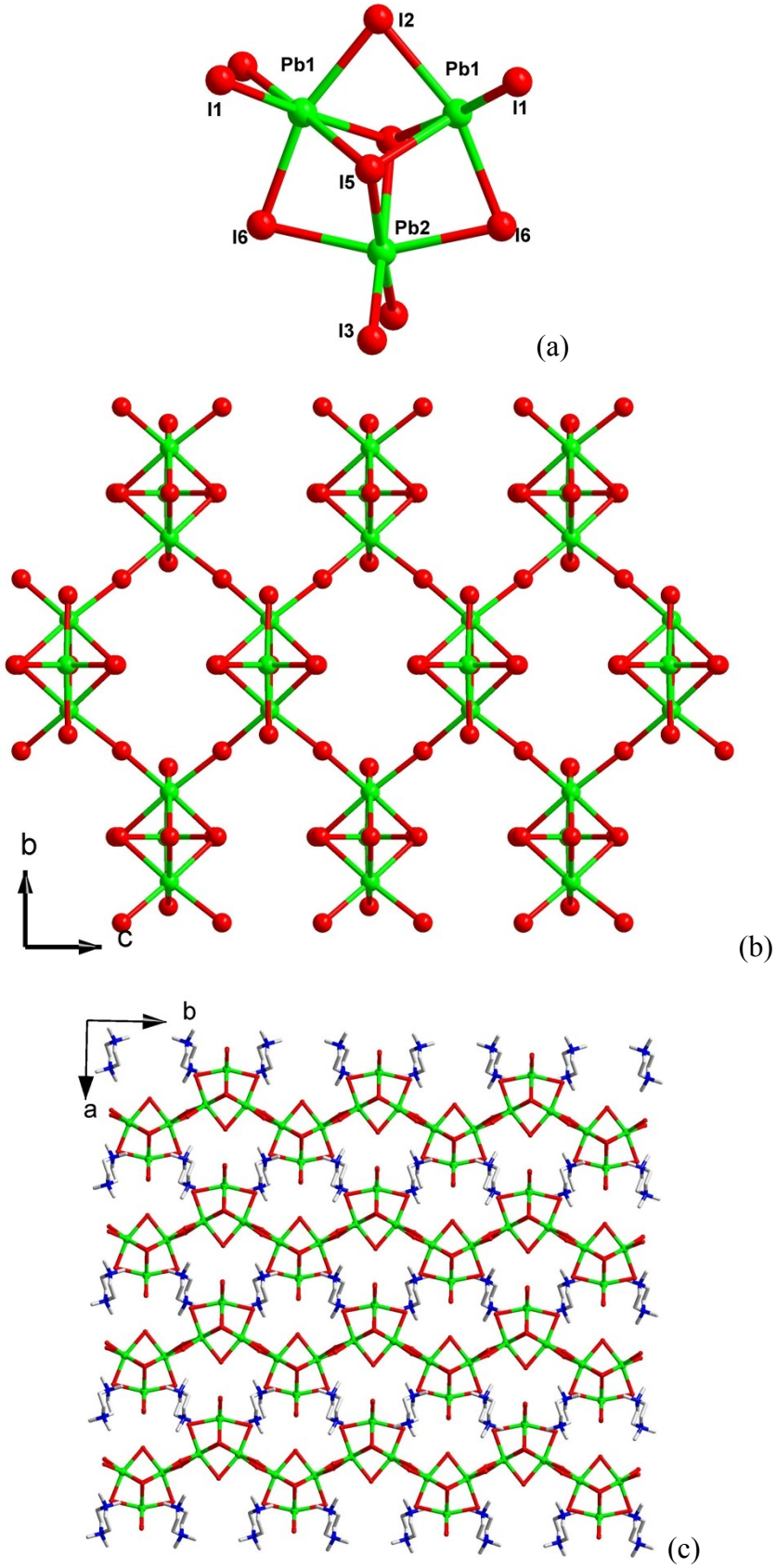

Fig. S6. Detailed view of $[Pb_3I_{11}]^{5-}$ trimer (a), the 2D corrugated $[Pb_3I_9]^{3-}$ layer (b), and the 3D packing structure of compound **5** (c).

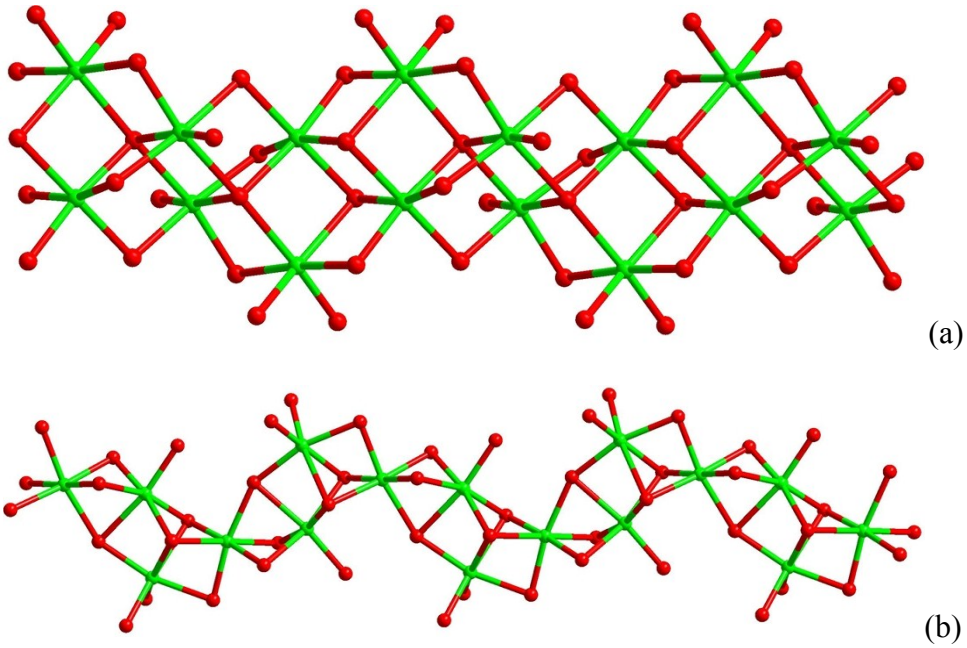

Fig. S7. The 1D $[Pb_3I_9]^{3-}$ chains in compound $[EV]_{1.5}[Pb_3I_9]$ (a) and $(tbpm)[Pb_3I_9]\cdot H_2O$ (b).

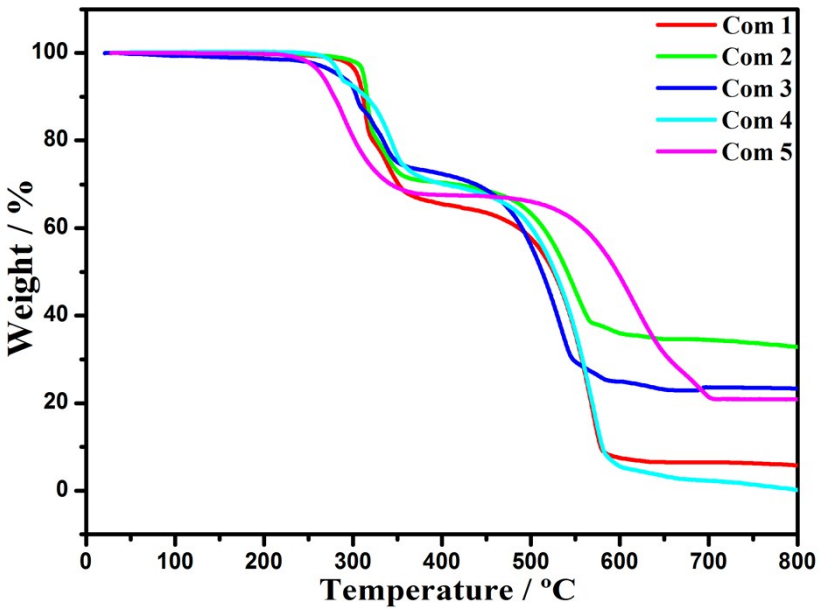

Fig. S8. The thermogravimetric analyses (TGA) curves for compounds **1**−**5**.

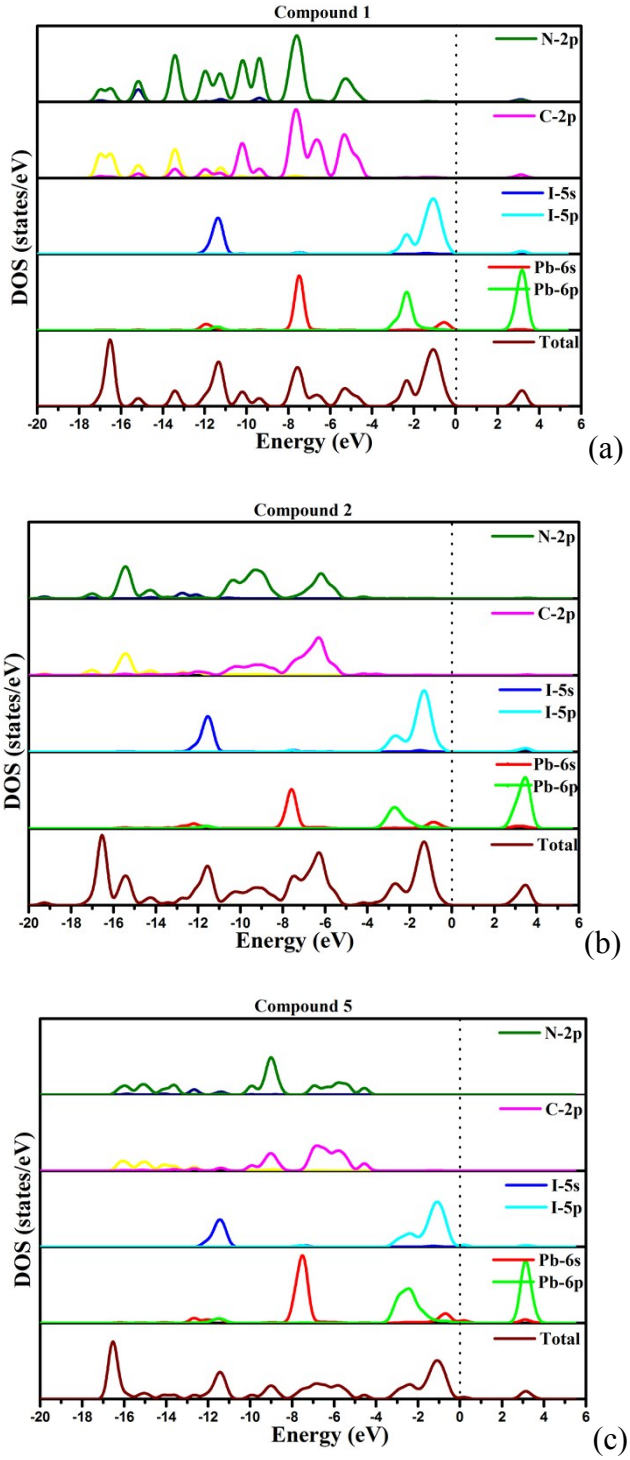

Fig. **S9**. The total and partial density of states for compounds **1** (a), **2** (b) and **5** (c).

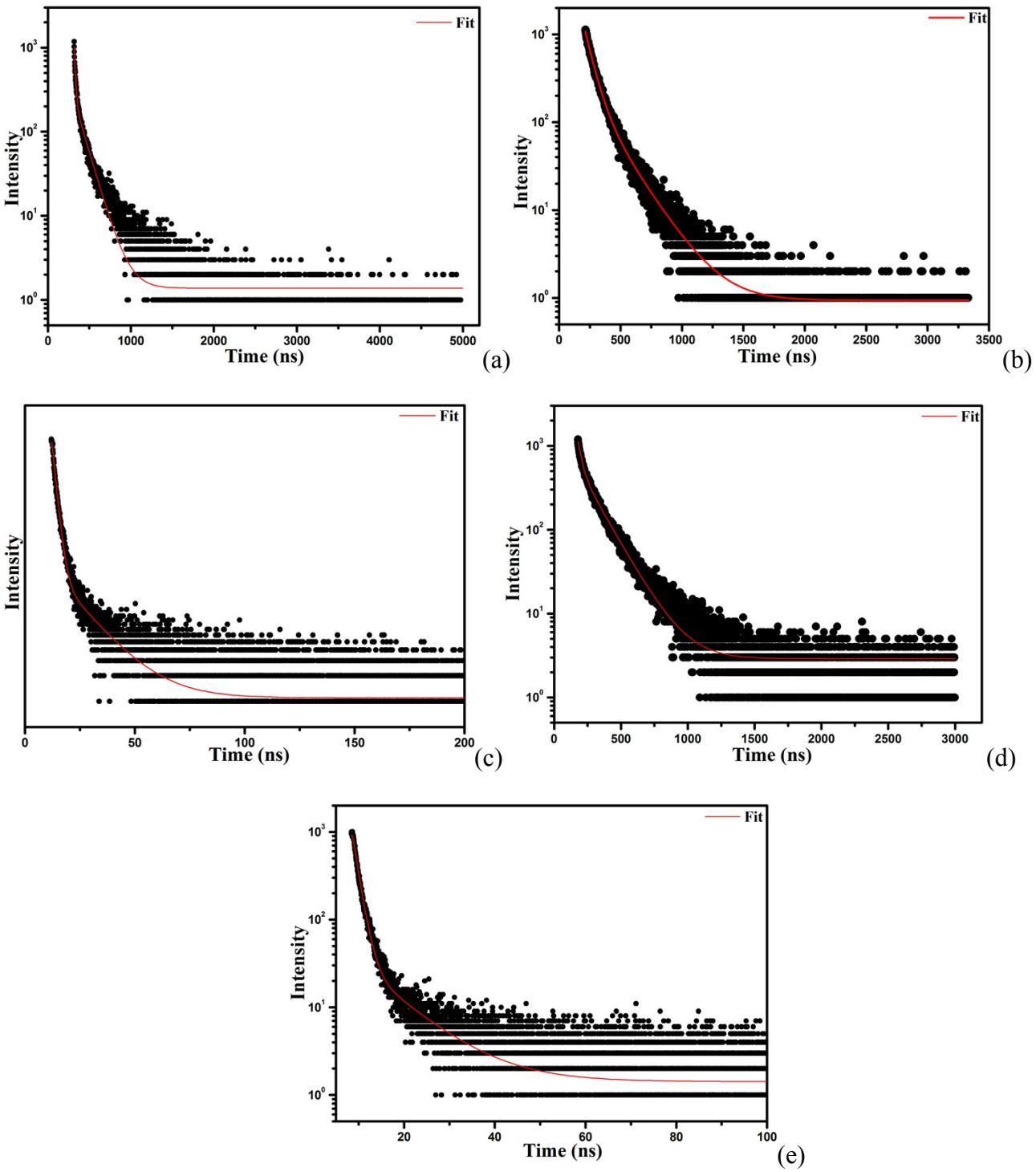

Fig. **S10**. The photoluminescence decay data and fitting curve of compounds **1** (a), **2** (b), **3** (c), **4** (d) and **5** (e) measured at room temperature.

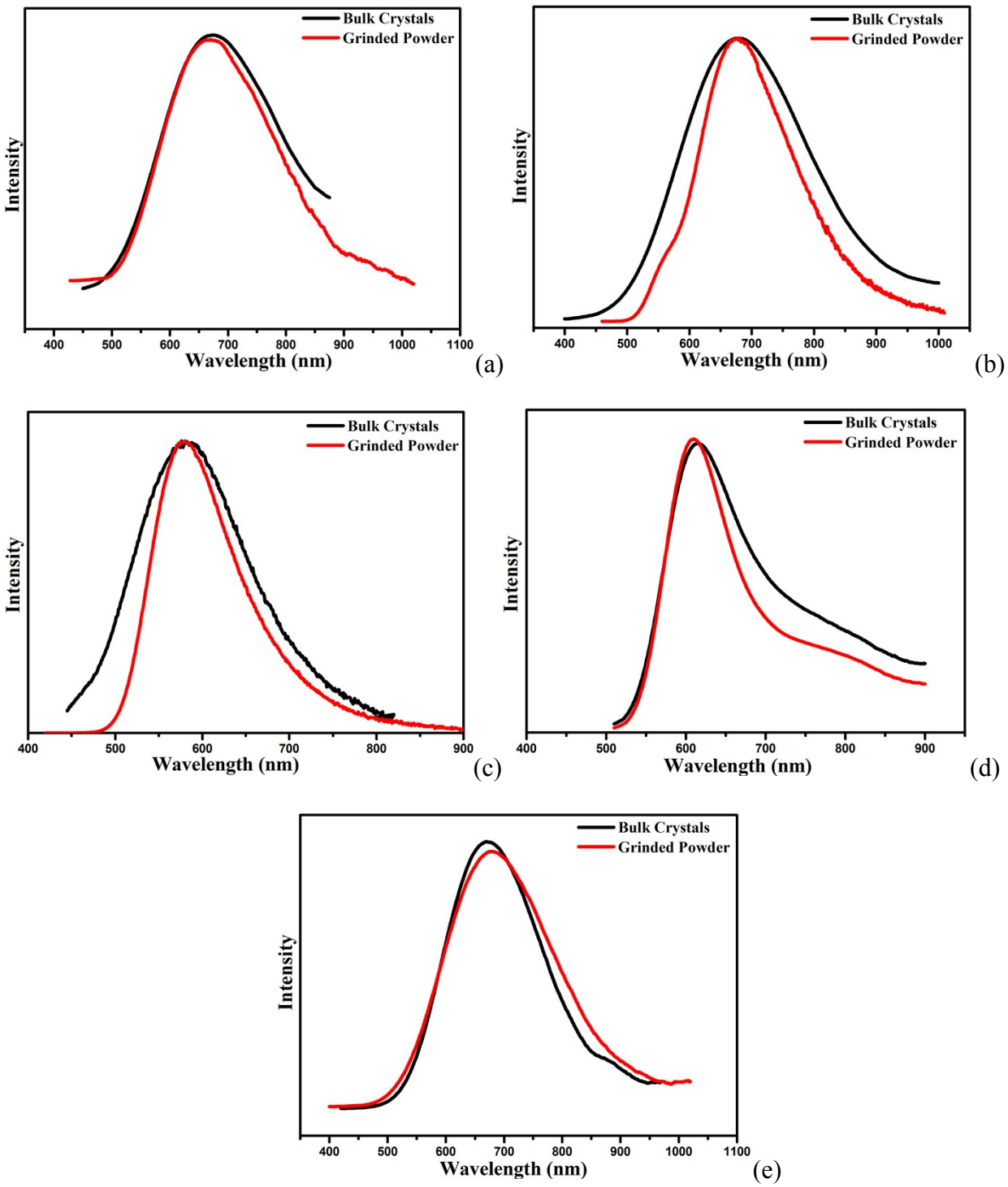

Fig. **S11**. Photoluminescence of bulk crystals and grinded powder for compounds **1** (a), **2** (b), **3** (c), **4** (d) and **5** (e) measured at room temperature.

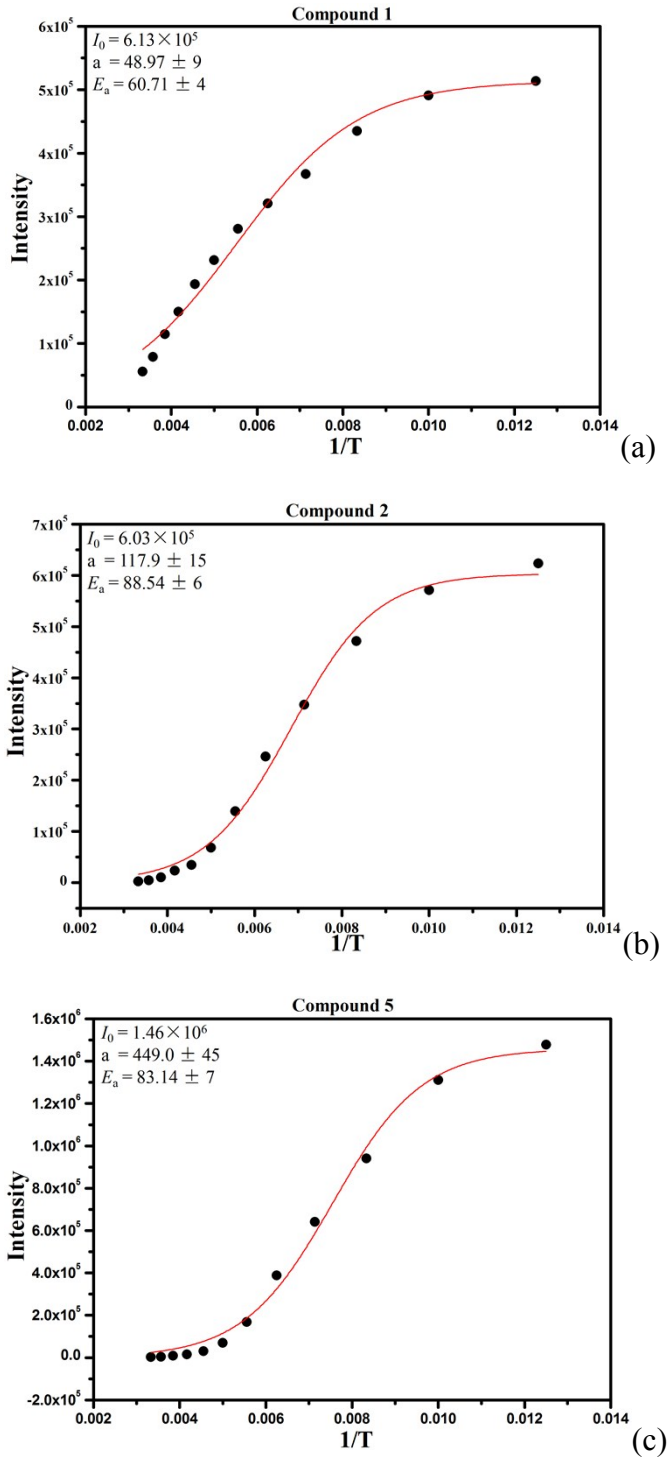

Fig. S12. Temperature dependence of PL intensity and the theoretical fitting data from Arrhenius-type model for compounds **1** (a), **2** (b) and **5** (c).

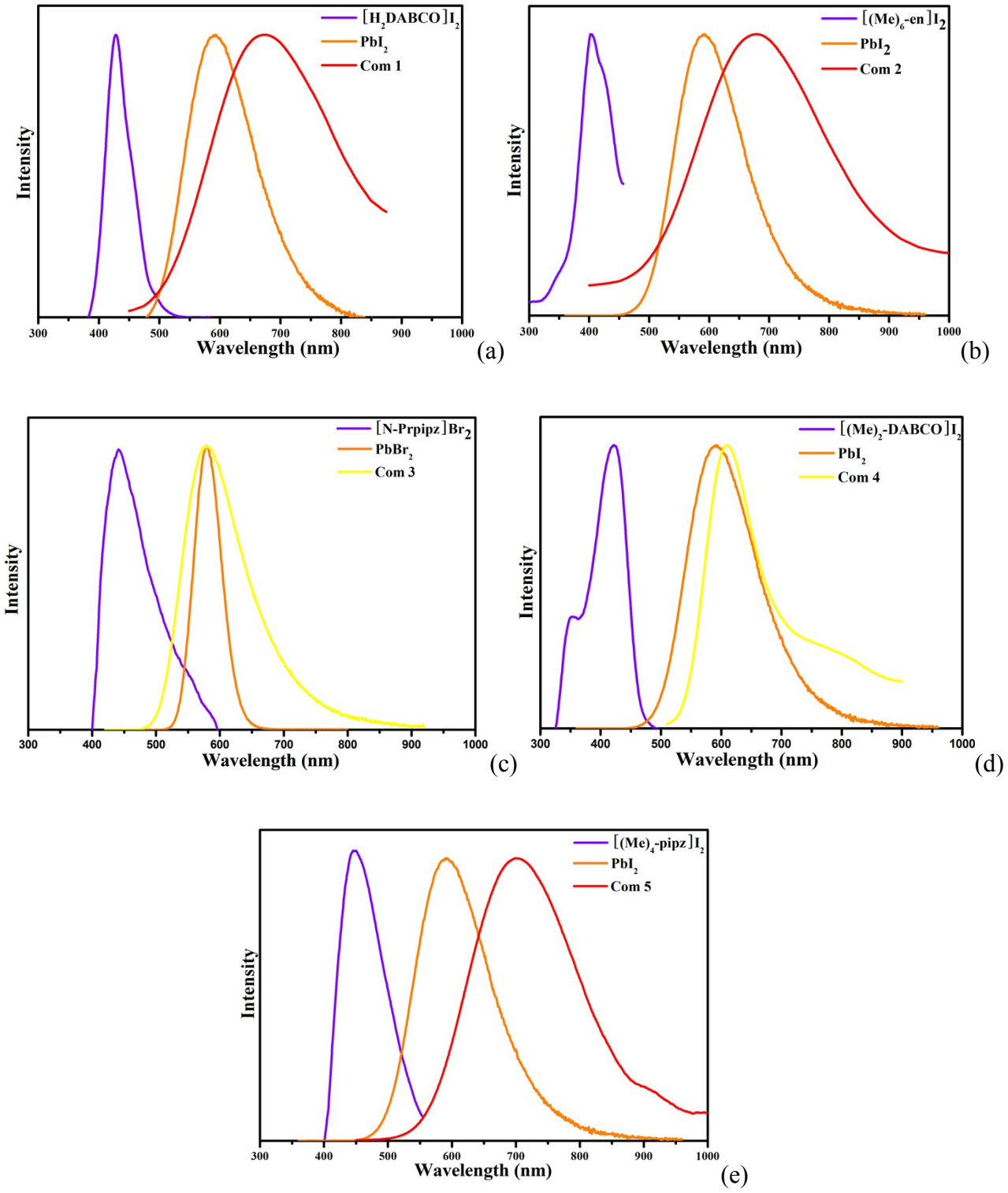

Fig. **S13**. Comparison of room-temperature PL emission spectra of compounds **1-5** with the primary materials and organic salts. Spectra are normalized for clarity.

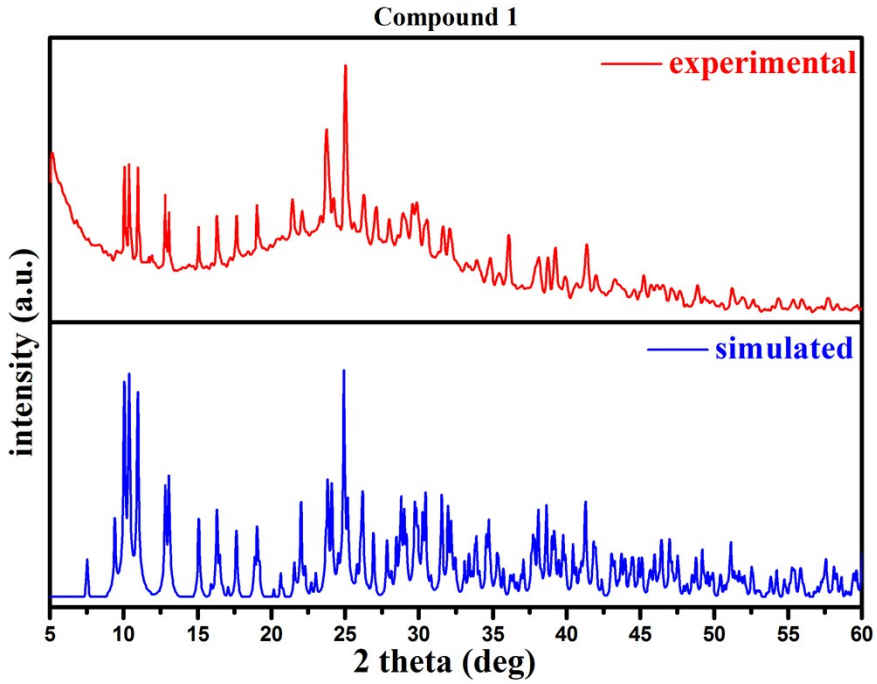

Fig. S14. The experimental and simulated XRD patterns of compound **1**.

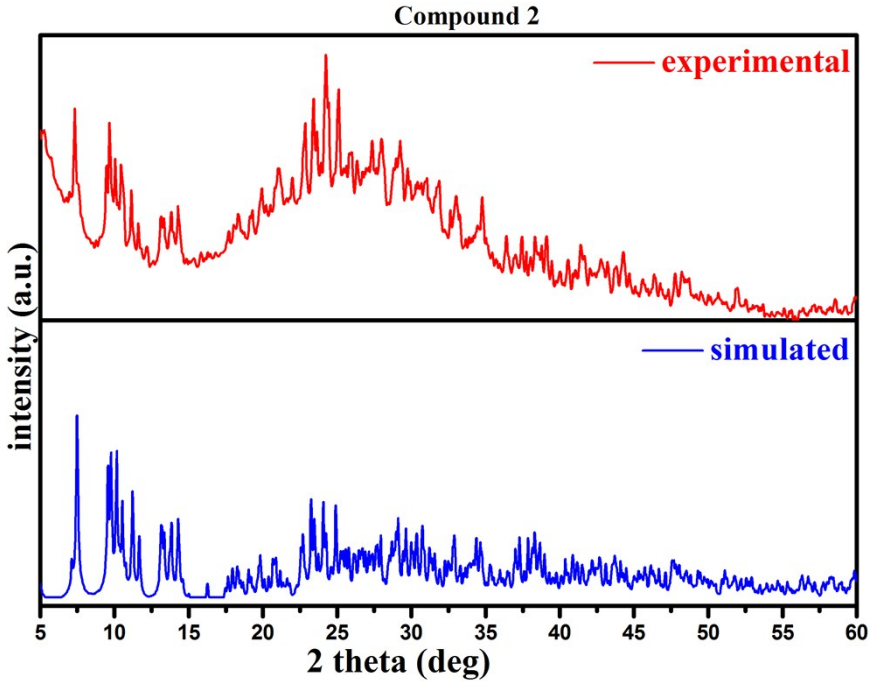

Fig. S15. The experimental and simulated XRD patterns of compound **2**.

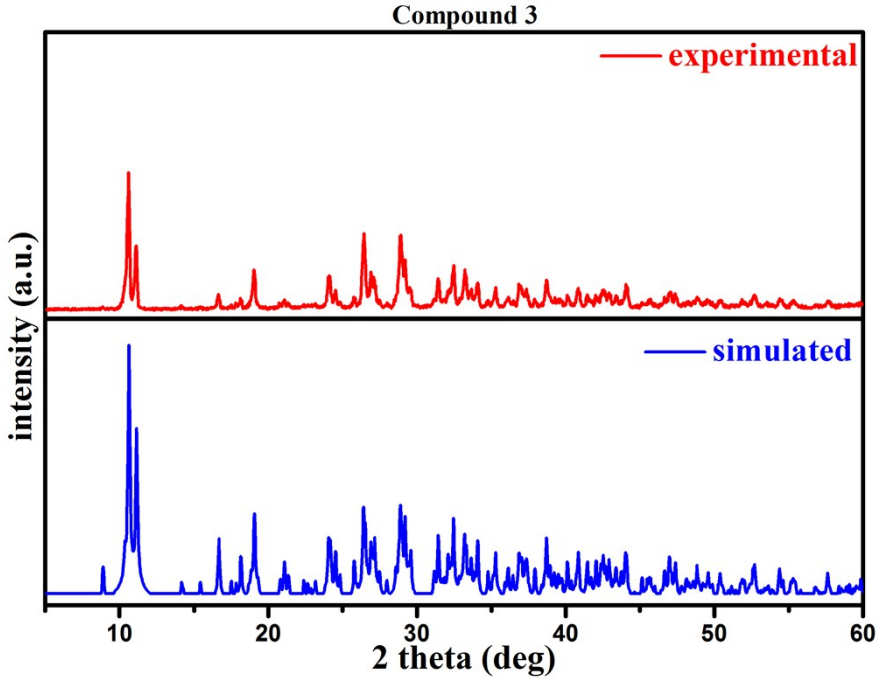

Fig. S16. The experimental and simulated XRD patterns of compound **3**.

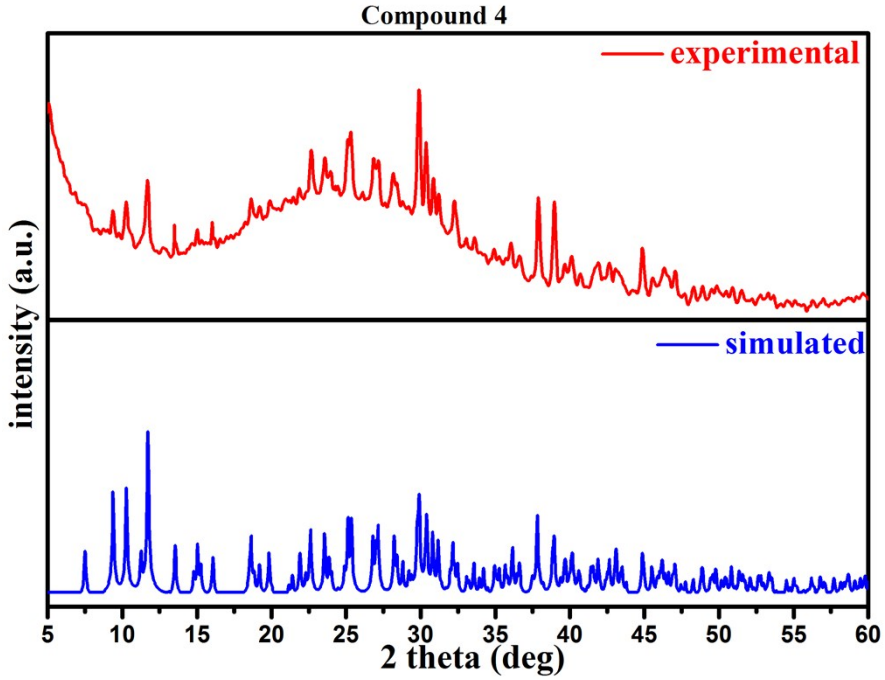

Fig. S17. The experimental and simulated XRD patterns of compound **4**.

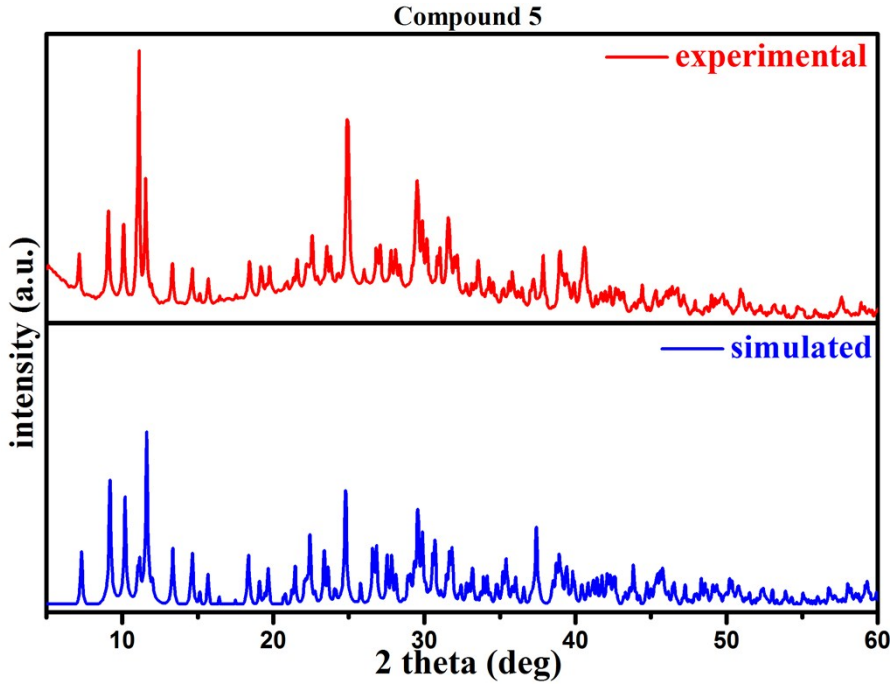

Fig. S18. The experimental and simulated XRD patterns of compound **5**.

Table S1. Crystal Data and Structure Refinements for compounds **1-3**.

Compound	**1**	**2**	**3**
chemical formula	$C_{16}H_{44}N_6Pb_3I_{12}$	$C_{16}N_4H_{44}Pb_3I_{10}$	$C_{14}N_6H_{38}Pb_3Br_{10}$
fw	2464.94	2183.12	1711.17
Space group	$P2_1/c$	P-1	$P2_1/c$
a/Å	12.450(3)	9.5123(8)	11.270(3)
b/Å	11.127(3)	13.4417(12)	15.861(4)
c/Å	18.665(5)	19.1192(17)	11.479(3)
$\alpha/^o$	90	75.6650(10)	90
$\beta/^o$	109.395(4)	89.9240(10)	118.201(3)
$\gamma/^o$	90	72.4660(10)	90
V(Å^3)	2432.4(3)	2251.3(3)	1808.2(9)
Z	2	2	2
D_{calcd} (g·cm^{-3})	3.357	3.220	3.143
Temp (K)	298	298	298
μ (mm^{-1})	17.942	18.059	24.997
F(000)	2128	1888	1520
Reflections collected	18695	26362	6832
Unique reflections	5401	10146	3386
Reflections ($I>2\sigma(I)$)	3680	8128	2322
GOF on F^2	1.031	1.037	1.020
R_1,wR_2 ($I > 2\sigma(I)$)[a]	0.0481/ 0.1382	0.0366/0.0824	0.0578/0.1334
R_1,wR_2 (all data)	0.0600/ 0.1422	0.0505/0.0872	0.0676/0.1350
$\Delta\rho_{max}$ (e/Å^3)	1.785	2.832	4.417
$\Delta\rho_{min}$ (e/Å^3)	-1.483	-1.134	-3.935

Table S2. Crystal Data and Structure Refinements for compounds **4-5**.

Compound	**4**	**5**
chemical formula	$C_8N_2H_{19}Pb_3I_9$	$C_8N_2H_{21}Pb_3I_9$
fw	1906.92	1908.94
Space group	$C222_1$	*Pnma*
a/Å	9.2418(14)	24.171(6)
b/Å	23.535(4)	15.841(4)
c/Å	15.709(2)	9.290(2)
V(Å^3)	3417.0(9)	3557.1(15)
Z	4	4
D_{calcd} (g·cm^{-3})	3.707	3.565
Temp (*K*)	298	298
μ (mm^{-1})	22.876	21.975
F(000)	3216	3224
Reflections collected	19563	17566
Unique reflections	3899	3229
Reflections ($I>2\sigma(I)$)	3471	2491
GOF on F^2	0.974	1.003
R_1,wR_2 ($I > 2\sigma(I)$)[a]	0.0340/0.0794	0.0379/0.0839
R_1,wR_2 (all data)	0.0391/0.0816	0.0433/0.0858
$\Delta\rho_{max}$ (e/Å^3)	1.785	2.776
$\Delta\rho_{min}$ (e/Å^3)	-4.362	-1.616

Table S3. Selected bond lengths (Å) for compound **1**.

Pb(1)-I(4)	3.2211(12)	Pb(2)-I(6)	3.0786(11)
Pb(1)-I(4)#1	3.2211(12)	Pb(2)-I(1)	3.1478(11)
Pb(1)-I(5)	3.2391(12)	Pb(2)-I(2)	3.1746(13)
Pb(1)-I(5)#1	3.2391(12)	Pb(2)-I(4)	3.3197(14)
Pb(1)-I(3)#1	3.2552(11)	Pb(2)-I(5)#1	3.3569(12)
Pb(1)-I(3)	3.2552(11)	Pb(2)-I(3)	3.4185(11)

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

Table S4. Selected bond lengths (Å) for compound **2**.

Pb(1)-I(11)	3.1673(6)	Pb(2)-I(1)	3.0867(8)
Pb(1)-I(10)	3.1952(7)	Pb(2)-I(7)	3.1173(7)
Pb(1)-I(4)	3.2548(4)	Pb(2)-I(6)	3.1834(8)
Pb(1)-I(3)	3.2550(4)	Pb(2)-I(11)	3.3106(7)
Pb(1)-I(9)	3.2811(8)	Pb(2)-I(9)	3.3594(8)
Pb(1)-I(8)	3.3069(8)	Pb(2)-I(10)	3.3906(7)
Pb(3)-I(5)	3.0818(7)	Pb(3)-I(10)	3.3360(7)
Pb(3)-I(2)	3.1048(8)	Pb(3)-I(6)	3.3444(8)
Pb(3)-I(8)	3.2250(8)		

Table S5. Selected bond lengths (Å) for compound **3**.

Pb(1)-Br(4)	2.8631(19)	Pb(2)-Br(5)	3.0151(18)
Pb(1)-Br(1)#1	3.0278(16)	Pb(2)-Br(5)#2	3.0151(18)
Pb(1)-Br(2)	3.0286(17)	Pb(2)-Br(2)	3.0425(17)
Pb(1)-Br(3)	3.0637(16)	Pb(2)-Br(2)#2	3.0426(17)
Pb(1)-Br(1)	3.0949(17)	Pb(2)-Br(3)	3.0495(16)
Pb(1)-Br(5)	3.1607(19)	Pb(2)-Br(3)#2	3.0495(16)

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

Table S6. Selected bond lengths (Å) for compound **4**.

Pb(1)-I(3)	3.0300(8)	Pb(2)-I(1)#2	3.1609(10)
Pb(1)-I(3)#1	3.0300(8)	Pb(2)-I(4)	3.164(10)
Pb(1)-I(2)	3.2959(9)	Pb(2)-I(1)	3.1730(10)
Pb(1)-I(2)#1	3.2959(10)	Pb(2)-I(2)	3.1868(10)
Pb(1)-I(5)#1	3.4246(8)	Pb(2)-I(5)	3.2758(9)
Pb(1)-I(5)	3.4246(8)	Pb(2)-I(5)#1	3.2811(8)

Symmetry transformations used to generate equivalent atoms: #1 -*x*+2, *y*, -*z*+3/2, #2 *x*+1/2, -*y*+7/2, -*z*+2.

Table S7. Selected bond lengths (Å) for compound **5**.

Pb(1)-I(1)	3.1759(10)	Pb(2)-I(4)	3.0457(13)
Pb(1)-I(1)#1	3.1785(9)	Pb(2)-I(3)	3.0509(13)
Pb(1)-I(6)	3.2195(11)	Pb(2)-I(6)	3.2768(10)
Pb(1)-I(7)	3.2355(9)	Pb(2)-I(6)#2	3.2768(10)
Pb(1)-I(2)	3.2585(12)	Pb(2)-I(5)	3.4105(13)
Pb(1)-I(5)	3.2705(9)	Pb(2)-I(4)	3.0457(13)

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