Electronic Supporting Information (ESI) for:

Hybrid Iodoplumbates with Metal Complexes: Syntheses, Crystal Structures, Band Gaps and Photoelectric Properties

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1. Selected Bond Lengths and Bond Angles

Table S1. Selected bond lengths (Å) and bond angles (°) for compound **1**.

Pb(1)−I(1)	3.0169(6)	Pb(2)−I(4)#2	3.2333(4)
Pb(1)−I(2)#1	3.1880(4)	Pb(2)−I(4)	3.2333(4)
Pb(1)−I(2)	3.2266(5)	Pb(3)−O(2)	2.658(6)
Pb(1)−I(4)	3.2383(5)	Pb(3)−O(2)#3	2.658(6)
Pb(1)−I(3)	3.2962(5)	Pb(3)−O(4)	2.707(5)
Pb(1)−I(5)	3.4397(5)	Pb(3)−O(4)#3	2.707(5)
Pb(2)−I(5)#2	3.1794(4)	Pb(3)−O(3)	2.733(6)
Pb(2)−I(5)	3.1794(4)	Pb(3)−O(3)#3	2.733(6)
Pb(2)−I(3)	3.2100(4)	Pb(3)−O(1)#3	2.759(5)
Pb(2)−I(3)#2	3.2100(4)	Pb(3)−O(1)	2.759(5)
I(1)−Pb(1)−I(2)#1	95.155(16)	I(5)#2−Pb(2)−I(5)	180.0
I(1)−Pb(1)−I(2)	95.105(15)	I(5)#2−Pb(2)−I(3)	87.455(11)
I(2)#1−Pb(1)−I(2)	100.551(7)	I(5)−Pb(2)−I(3)	92.545(11)
I(1)−Pb(1)−I(4)	87.169(16)	I(5)#2−Pb(2)−I(3)#2	92.546(11)
I(2)#1−Pb(1)−I(4)	95.177(14)	I(5)−Pb(2)−I(3)#2	87.454(11)
I(2)−Pb(1)−I(4)	163.824(14)	I(3)−Pb(2)−I(3)#2	180.0
I(1)−Pb(1)−I(3)	97.427(17)	I(5)#2−Pb(2)−I(4)#2	91.444(11)
I(2)#1−Pb(1)−I(3)	167.077(14)	I(5)−Pb(2)−I(4)#2	88.556(11)
I(2)−Pb(1)−I(3)	81.282(13)	I(3)−Pb(2)−I(4)#2	96.021(12)
I(4)−Pb(1)−I(3)	82.543(13)	I(3)#2−Pb(2)−I(4)#2	83.978(12)
I(1)−Pb(1)−I(5)	172.323(14)	I(5)#2−Pb(2)−I(4)	88.556(11)
I(2)#1−Pb(1)−I(5)	80.648(11)	I(5)−Pb(2)−I(4)	91.444(11)

I(2)−Pb(1)−I(5)	91.997(11)	I(3)−Pb(2)−I(4)	83.979(12)
I(4)−Pb(1)−I(5)	86.816(11)	I(3)#2−Pb(2)−I(4)	96.021(12)
I(3)−Pb(1)−I(5)	86.516(12)	I(4)#2−Pb(2)−I(4)	180.0
O(2)−Pb(3)−O(2)#3	100.4(3)	O(3)−Pb(3)−O(3)#3	92.5(2)
O(2)−Pb(3)−O(4)	70.31(19)	O(2)−Pb(3)−O(1)#3	133.02(17)
O(2)#3−Pb(3)−O(4)	112.9(2)	O(2)#3−Pb(3)−O(1)#3	47.89(17)
O(2)−Pb(3)−O(4)#3	112.9(2)	O(4)−Pb(3)−O(1)#3	89.89(18)
O(2)#3−Pb(3)−O(4)#3	70.31(19)	O(4)#3−Pb(3)−O(1)#3	90.07(18)
O(4)−Pb(3)−O(4)#3	175.3(2)	O(3)−Pb(3)−O(1)#3	70.24(17)
O(2)−Pb(3)−O(3)	115.7(2)	O(3)#3−Pb(3)−O(1)#3	108.99(17)
O(2)#3−Pb(3)−O(3)	116.88(18)	O(2)−Pb(3)−O(1)	47.89(17)
O(4)−Pb(3)−O(3)	47.95(15)	O(2)#3−Pb(3)−O(1)	133.02(17)
O(4)#3−Pb(3)−O(3)	127.82(16)	O(4)−Pb(3)−O(1)	90.07(18)
O(2)−Pb(3)−O(3)#3	116.88(18)	O(4)#3−Pb(3)−O(1)	89.89(18)
O(2)#3−Pb(3)−O(3)#3	115.7(2)	O(3)−Pb(3)−O(1)	108.99(17)
O(4)−Pb(3)−O(3)#3	127.83(16)	O(3)#3−Pb(3)−O(1)	70.24(17)
O(4)#3−Pb(3)−O(3)#3	47.95(15)	O(1)#3−Pb(3)−O(1)	178.9(2)

Symmetry codes: #1 −*x*+3/2, *y*, *z*+1/2; #2 −*x*+1, −*y*+1, −*z*+1; #3 −*x*+1/2, −*y*+3/2, *z*.

Table S2. Hydrogen bonds (Å) and angles (º) for compound **1**.

D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
C(5)−H(5A)···I(2)#5	0.96	3.21	3.775(7)	119.0
C(7)−H(7)···I(1)#4	0.93	3.25	3.889(7)	128.0
C(10)−H(10)···I(5)#2	0.93	3.05	3.760(6)	134.6
C(12)−H(12B)···I(4)#6	0.96	3.22	3.770(7)	118.6

Symmetry codes: #2 −*x*+1, −*y*+1, −*z*+1; #4 *x*, −*y*+3/2, *z*+1/2; #5 −*x*+3/2, −*y*+3/2, *z*; #6 −*x*+1, −*y*+1, −*z*+2.

Table S3. Anion···π interactions [Å and °] for compound **1**.

Y−X···Cg	*d*(X···Cg)	∠(Y−X···Cg)
Pb(1)−I(1)···Cg(1)#7	3.719(3)	155.31(5)

Symmetry codes: #7 *x*, *y*, *z*.

Cg(1): N(1)−C(4)−C(3)−C(2)−C(7)−C(6).

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

Pb(1)−I(3)	2.9413(5)	Pb(2)−I(6)	2.9457(6)
Pb(1)−I(4)	3.1726(5)	Pb(2)−I(2)#1	3.1856(6)
Pb(1)−I(5)	3.2006(6)	Pb(2)−I(1)#1	3.2106(5)
Pb(1)−I(2)	3.2775(5)	Pb(2)−I(5)	3.2467(6)
Pb(1)−I(1)	3.2812(5)	Pb(2)−I(4)	3.3422(5)
Co(1)−N(6)	2.121(5)	Co(1)−N(1)	2.130(5)
Co(1)−N(2)	2.125(5)	Co(1)−N(4)	2.160(5)
Co(1)−N(3)	2.125(5)	Co(1)−N(5)	2.169(5)
I(3)−Pb(1)−I(4)	94.453(15)	I(6)−Pb(2)−I(2)#1	98.902(18)
I(3)−Pb(1)−I(5)	97.384(18)	I(6)−Pb(2)−I(1)#1	92.555(15)
I(4)−Pb(1)−I(5)	89.507(15)	I(2)#1−Pb(2)−I(1)#1	91.233(15)

I(3)−Pb(1)−I(2)	88.116(16)	I(6)−Pb(2)−I(5)	98.12(2)
I(4)−Pb(1)−I(2)	175.869(14)	I(2)#1−Pb(2)−I(5)	161.70(2)
I(5)−Pb(1)−I(2)	86.953(15)	I(1)#1−Pb(2)−I(5)	94.694(16)
I(3)−Pb(1)−I(1)	87.796(16)	I(6)−Pb(2)−I(4)	82.176(14)
I(4)−Pb(1)−I(1)	94.952(13)	I(2)#1−Pb(2)−I(4)	89.851(13)
I(5)−Pb(1)−I(1)	172.898(18)	I(1)#1−Pb(2)−I(4)	174.724(15)
I(2)−Pb(1)−I(1)	88.371(13)	I(5)−Pb(2)−I(4)	85.833(13)
N(6)−Co(1)−N(2)	96.62(18)	N(3)−Co(1)−N(4)	77.87(18)
N(6)−Co(1)−N(3)	163.86(18)	N(1)−Co(1)−N(4)	96.7(2)
N(2)−Co(1)−N(3)	95.26(19)	N(6)−Co(1)−N(5)	77.86(17)
N(6)−Co(1)−N(1)	97.26(18)	N(2)−Co(1)−N(5)	98.48(19)
N(2)−Co(1)−N(1)	78.7(2)	N(3)−Co(1)−N(5)	89.62(18)
N(3)−Co(1)−N(1)	95.75(19)	N(1)−Co(1)−N(5)	174.13(19)
N(6)−Co(1)−N(4)	91.13(17)	N(4)−Co(1)−N(5)	86.70(19)
N(2)−Co(1)−N(4)	171.43(18)		

Symmetry codes: #1 −*x*+3/2, *y*+1/2, *z*.

Table S5. Hydrogen bonds (Å) and angles (º) for compound **2**.

D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
C(14)−H(14)···I(4)#2	0.93	3.10	3.810(6)	134.4
C(36)−H(36)···I(4)#3	0.93	3.07	3.738(6)	130.3
C(38)−H(38C)···I(5)#4	0.96	3.03	3.86(4)	146.5

Symmetry codes: #2 −*x*+1, *y*−1/2, −*z*+1/2; #3 −*x*+1, −*y*+1, −*z*+1; #4 *x*−1/2, *y*, −*z*+1/2.

Table S6. Anion···π interactions [Å and °] for compound **2**.

Y−X···Cg	*d*(X···Cg)	∠(Y−X···Cg)
Pb(2)−I(6)···Cg(1)#5	3.997(4)	116.51(6)

Symmetry codes: #5 1−*x*, 1/2+*y*, 1/2−*z*.
Cg(1): C(4)−C(5)−C(9)−C(8)−C(7)−C(6).

Table S7. Selected bond lengths (Å) and bond angles (°) for compound **3**.

Pb(1)−I(3)	3.0072(16)	Pb(2)−I(5)	3.2785(19)
Pb(1)−I(5)	3.1611(18)	Pb(2)−I(4)	3.4365(16)
Pb(1)−I(4)	3.1828(16)	Fe(1)−N(1)	1.964(16)
Pb(1)−I(2)	3.3035(18)	Fe(1)−N(3)	1.968(14)
Pb(1)−I(1)	3.3289(18)	Fe(1)−N(2)	1.978(16)
Pb(2)−I(6)	3.0025(17)	Fe(1)−N(6)	1.980(14)
Pb(2)−I(1)#1	3.1547(18)	Fe(1)−N(4)	1.998(14)
Pb(2)−I(2)#1	3.1972(19)	Fe(1)−N(5)	2.007(16)
I(3)−Pb(1)−I(5)	95.27(5)	I(6)−Pb(2)−I(1)#1	91.48(5)
I(3)−Pb(1)−I(4)	96.87(4)	I(6)−Pb(2)−I(2)#1	101.84(6)
I(5)−Pb(1)−I(4)	89.82(5)	I(1)#1−Pb(2)−I(2)#1	90.30(5)
I(3)−Pb(1)−I(2)	86.28(5)	I(6)−Pb(2)−I(5)	93.04(6)
I(5)−Pb(1)−I(2)	89.05(5)	I(1)#1−Pb(2)−I(5)	98.34(5)
I(4)−Pb(1)−I(2)	176.74(5)	I(2)#1−Pb(2)−I(5)	162.61(5)
I(3)−Pb(1)−I(1)	83.60(5)	I(6)−Pb(2)−I(4)	78.04(4)

I(5)−Pb(1)−I(1)	174.52(5)	I(1)#1−Pb(2)−I(4)	169.45(5)
I(4)−Pb(1)−I(1)	95.64(4)	I(2)#1−Pb(2)−I(4)	90.63(4)
I(2)−Pb(1)−I(1)	85.53(5)	I(5)−Pb(2)−I(4)	83.63(4)
N(1)−Fe(1)−N(3)	92.7(6)	N(2)−Fe(1)−N(4)	174.3(6)
N(1)−Fe(1)−N(2)	82.5(7)	N(6)−Fe(1)−N(4)	91.0(6)
N(3)−Fe(1)−N(2)	91.4(6)	N(1)−Fe(1)−N(5)	176.5(7)
N(1)−Fe(1)−N(6)	94.0(6)	N(3)−Fe(1)−N(5)	90.2(6)
N(3)−Fe(1)−N(6)	171.6(6)	N(2)−Fe(1)−N(5)	95.5(6)
N(2)−Fe(1)−N(6)	94.5(6)	N(6)−Fe(1)−N(5)	83.2(6)
N(1)−Fe(1)−N(4)	95.6(6)	N(4)−Fe(1)−N(5)	86.6(6)
N(3)−Fe(1)−N(4)	83.3(6)		

Symmetry codes: #1 −*x*+3/2, *y*+1/2, *z*.

Table S8. Hydrogen bonds (Å) and angles (º) for compound **3**.

D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
C(14)−H(14)···I(4)#3	0.93	3.08	3.853(10)	141.8
C(23)−H(23)···I(6)#2	0.93	3.21	3.821(10)	124.6
C(36)−H(36)···I(4)#4	0.93	3.11	3.729(9)	125.8

Symmetry codes: #2 −*x*+3/2, *y*−1/2, *z*; #3 −*x*+1, *y*−1/2, −*z*+1/2; #4 −*x*+1, −*y*+1, −*z*+1.

Table S9. C−H···π interactions [Å and ˚] for compound **3**.

X−H···Cg	*d*(H···Cg)	∠(X−H···Cg)
C(13)−H(13)···Cg(1)#5	2.93	140
C(24)−H(24)···Cg(2)#5	2.76	136
C(25)−H(25)···Cg(3)#5	2.82	135

Symmetry codes: #5 *x*, *y*, *z*.

Cg(1): N(2)−C(9)−C(8)−C(10)−C(11)−C(12); Cg(2): N(6)−C(30)−C(31)−C(34)−C(35)−C(36); Cg(3): N(3)−C(13)−C(14)−C(15)−C(16)−C(17).

Table S10. Selected bond lengths (Å) and bond angles (°) for compound **4**.

Pb(1)−I(3)	2.9604(8)	Pb(2)−I(6)	2.9575(9)
Pb(1)−I(4)	3.1673(8)	Pb(2)−I(1)#1	3.1794(8)
Pb(1)−I(5)	3.1779(8)	Pb(2)−I(2)#1	3.1871(9)
Pb(1)−I(2)	3.2883(8)	Pb(2)−I(5)	3.2600(9)
Pb(1)−I(1)	3.2979(8)	Pb(2)−I(4)	3.3788(7)
Ni(1)−N(2)	2.067(8)	Ni(1)−N(3)	2.081(7)
Ni(1)−N(1)	2.076(7)	Ni(1)−N(4)	2.101(7)
Ni(1)−N(6)	2.079(7)	Ni(1)−N(5)	2.123(7)
I(3)−Pb(1)−I(4)	95.24(2)	I(6)−Pb(2)−I(1)#1	92.01(2)
I(3)−Pb(1)−I(5)	96.38(3)	I(6)−Pb(2)−I(2)#1	99.72(3)
I(4)−Pb(1)−I(5)	89.77(2)	I(1)#1−Pb(2)−I(2)#1	91.25(2)
I(3)−Pb(1)−I(2)	87.66(2)	I(6)−Pb(2)−I(5)	96.64(3)
I(4)−Pb(1)−I(2)	176.37(2)	I(1)#1−Pb(2)−I(5)	95.90(2)
I(5)−Pb(1)−I(2)	87.74(2)	I(2)#1−Pb(2)−I(5)	161.89(3)
I(3)−Pb(1)−I(1)	86.08(2)	I(6)−Pb(2)−I(4)	80.60(2)
I(4)−Pb(1)−I(1)	94.96(2)	I(1)#1−Pb(2)−I(4)	172.61(2)

I(5)−Pb(1)−I(1)	174.46(3)	I(2)#1−Pb(2)−I(4)	90.24(2)
I(2)−Pb(1)−I(1)	87.41(2)	I(5)−Pb(2)−I(4)	84.80(2)
N(2)−Ni(1)−N(1)	80.0(3)	N(6)−Ni(1)−N(4)	91.3(3)
N(2)−Ni(1)−N(6)	96.2(3)	N(3)−Ni(1)−N(4)	79.0(3)
N(1)−Ni(1)−N(6)	96.3(3)	N(2)−Ni(1)−N(5)	97.5(3)
N(2)−Ni(1)−N(3)	94.1(3)	N(1)−Ni(1)−N(5)	174.9(3)
N(1)−Ni(1)−N(3)	94.3(3)	N(6)−Ni(1)−N(5)	79.5(3)
N(6)−Ni(1)−N(3)	166.3(3)	N(3)−Ni(1)−N(5)	90.2(3)
N(2)−Ni(1)−N(4)	171.9(3)	N(4)−Ni(1)−N(5)	87.0(3)
N(1)−Ni(1)−N(4)	96.1(3)		

Symmetry codes: #1 −*x*+3/2, *y*+1/2, *z*.

Table S11. Hydrogen bonds (Å) and angles (°) for compound **4**.

D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
C(14)−H(14)···I(4)#3	0.93	3.09	3.828(9)	137.7
C(23)−H(23)···I(6)#2	0.93	3.30	3.871(9)	121.7
C(25)−H(25)···N(3)	0.93	2.68	3.155(12)	112.5
C(36)−H(36)···I(4)#5	0.93	3.09	3.742(9)	128.7
C(38B)−H(38E)···I(2)#4	0.96	3.09	3.89(5)	141.0

Symmetry codes: #2 −*x*+3/2, *y*−1/2, *z*; #3 −*x*+1, *y*−1/2, −*z*+1/2; #4 *x*−1/2, *y*, −*z*+1/2; #5 −*x*+1, −*y*+1, −*z*+1.

Table S12. C−H···π interactions [Å and °] for compound **4**.

X−H···Cg	*d*(H···Cg)	∠(X−H···Cg)
C(24)−H(24)···Cg(3)#6	2.94	134
C(25)−H(25)···Cg(5)#6	2.88	136

Symmetry codes: #6 *x*, *y*, *z*.

Cg(3): N(6)−C(30)−C(31)−C(34)−C(35)−C(36); Cg(5): N(3)−C(13)−C(14)−C(15)−C(16)−C(17).

2. Crystal Structure

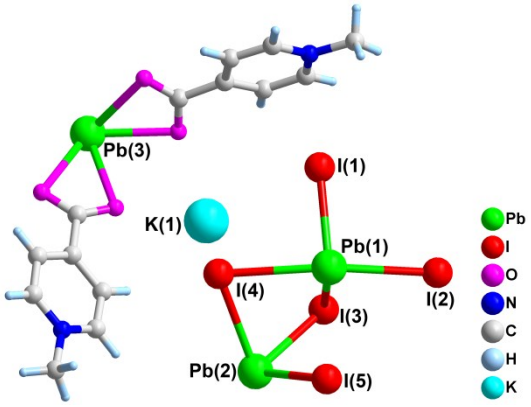

Fig. S1. The asymmetric unit of compound **1**.

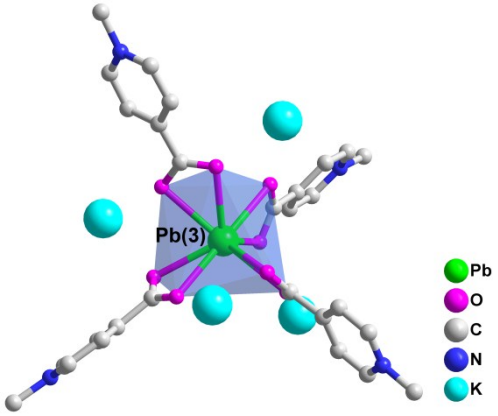

Fig. S2. Detailed view of the coordination environment between the $[Pb(3)(MCP)_4]^{2+}$ cation and the $K(1)^+$ ions for compound **1**.

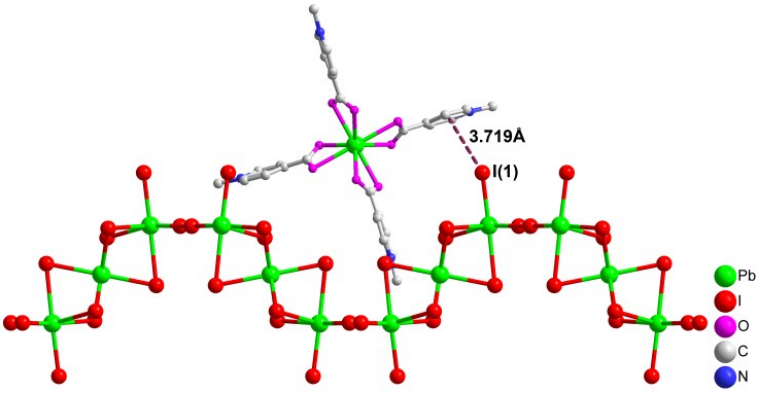

Fig. S3. The $[Pb(MCP)_4]^{2+}$ cation and bow-like $[Pb_3I_{10}]_n^{4n-}$ anionic layer with the Pb–I···π interactions for compound **1**.

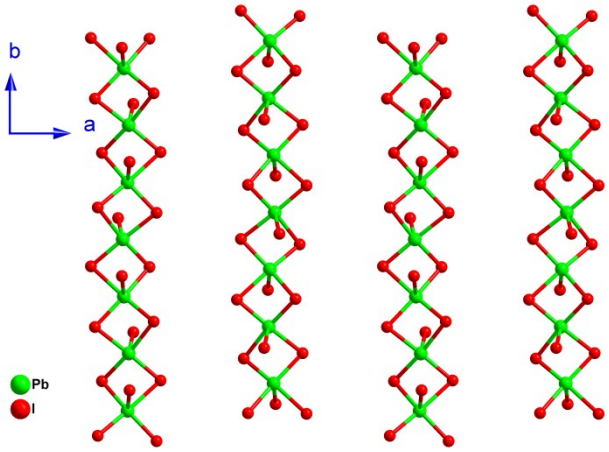

Fig. S4. View of the $[Pb_2I_6]^{2n-}$ anionic chains along the *c* axis for compound **2**.

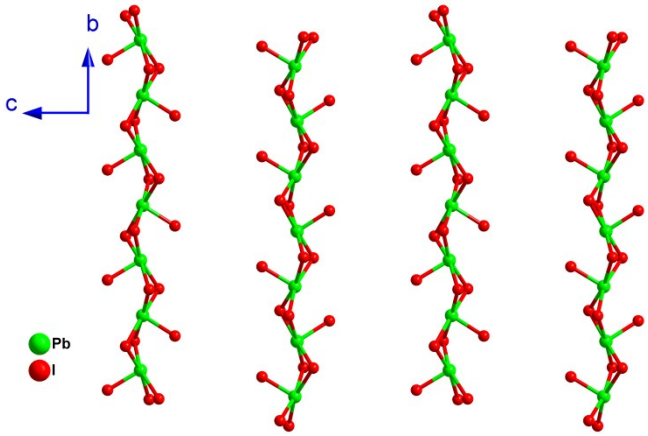

Fig. S5. View of the $[Pb_2I_6]^{2n-}$ anionic chains along the *a* axis for compound **2**.

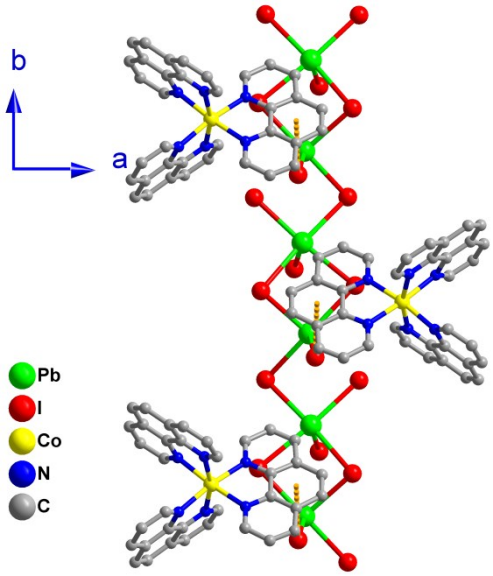

Fig. S6. The $[Co(phen)_3]^{2+}$ cations and the $[Pb_2I_6]_n^{2n-}$ anionic chain of compound **2**. Dashed lines show the anion···π interactions.

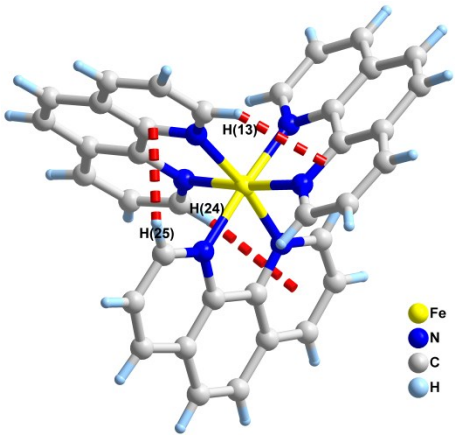

Fig. S7. The $[Fe(phen)_3]^{2+}$ cation of compound **3**. Dashed lines show the C−H···π interactions.

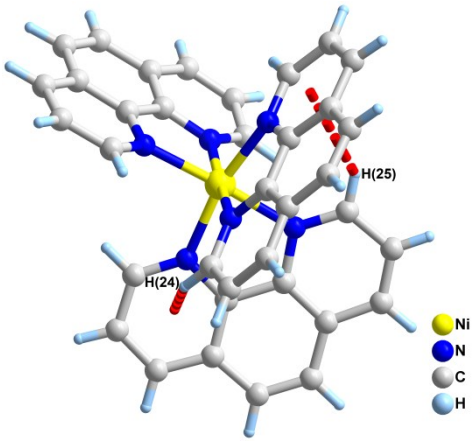

Fig. S8. The $[Ni(phen)_3]^{2+}$ cation of compound **4**. Dashed lines show the C−H···π interactions.

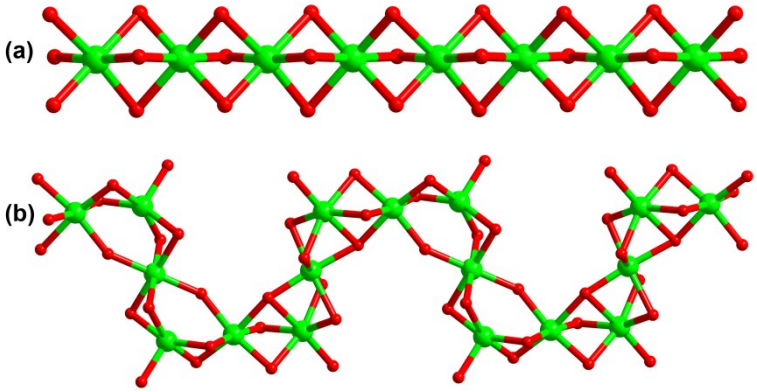

Fig. S9. The $[Pb_2I_6]_n^{2n-}$ (a) and $[Pb_2Br_6]_n^{2n-}$ (b) anionic chains in the literature.[1-2] The green and red balls represent the Pb and the X (X = I, Br) atoms, respectively.

3. Physical Measurements

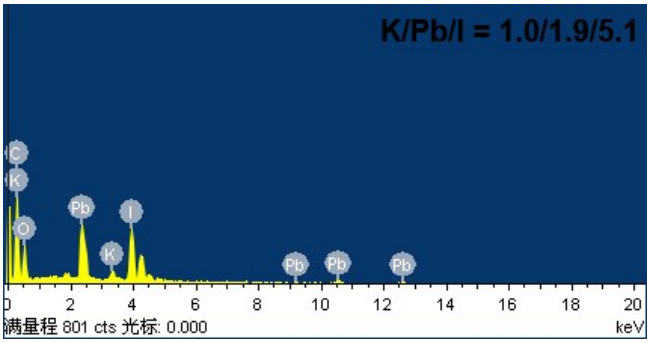

Fig. S10. The energy dispersive X-ray (EDX) spectrum of compound **1**.

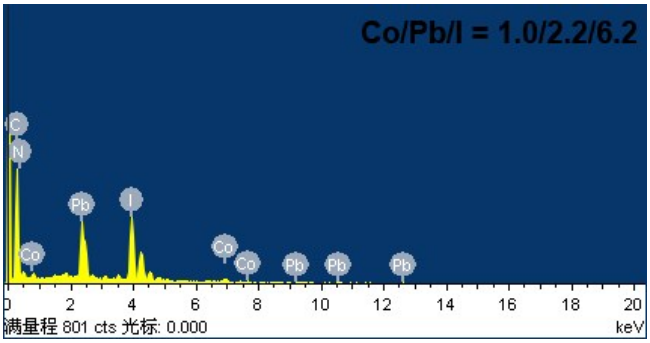

Fig. S11. The energy dispersive X-ray (EDX) spectrum of compound **2**.

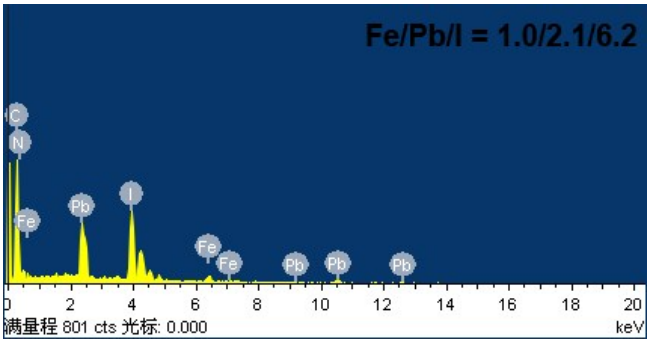

Fig. S12. The energy dispersive X-ray (EDX) spectrum of compound **3**.

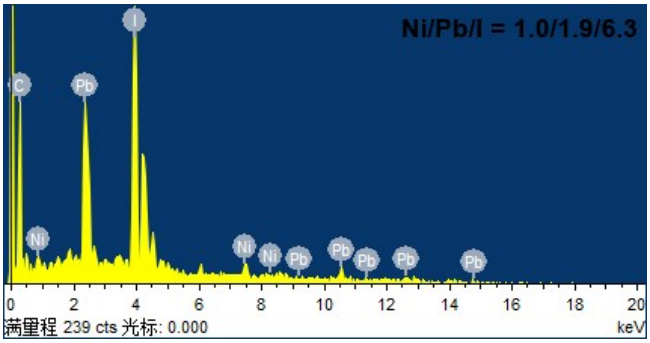

Fig. S13. The energy dispersive X-ray (EDX) spectrum of compound **4**.

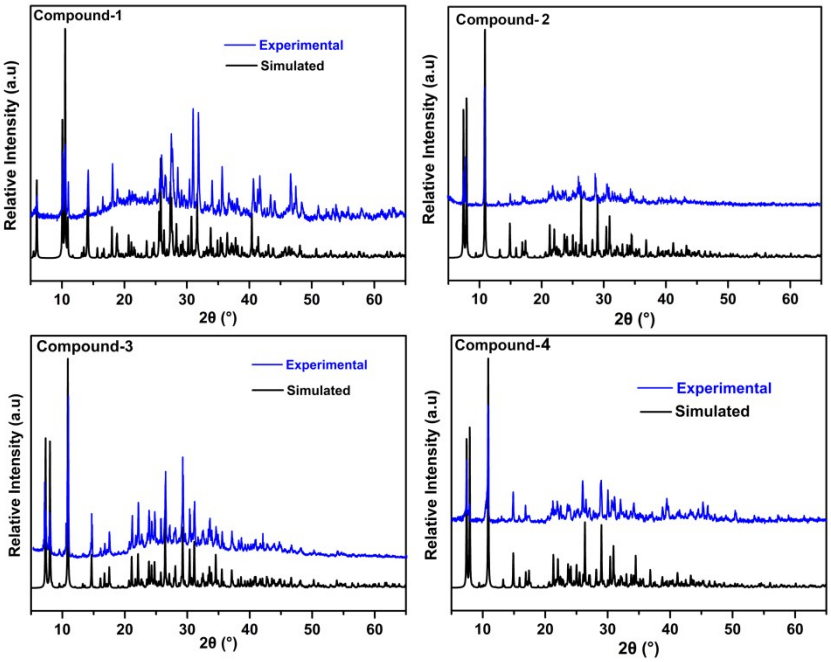

Fig. S14. PXRD patterns of compounds **1**−**4**.

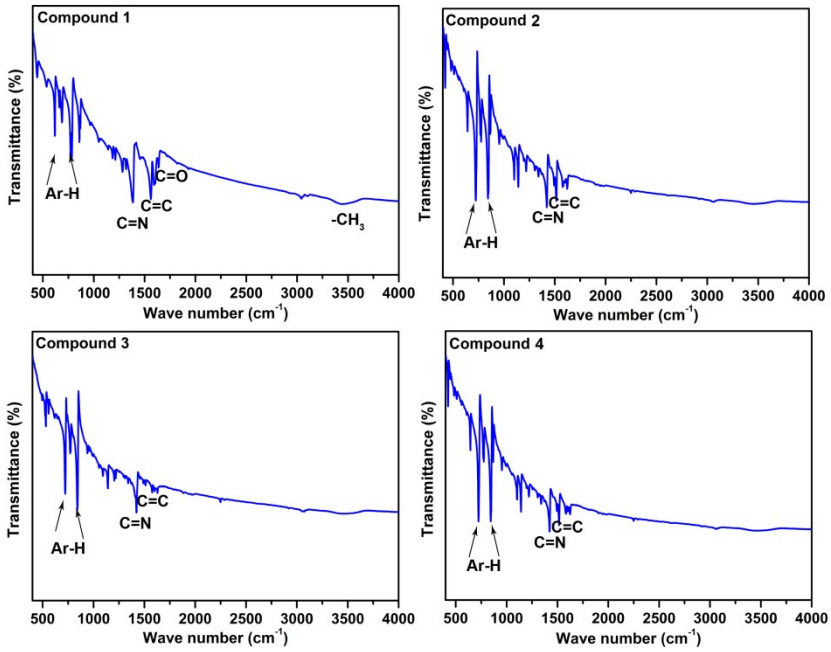

Fig. S15. FT−IR spectra of compounds **1**−**4**.

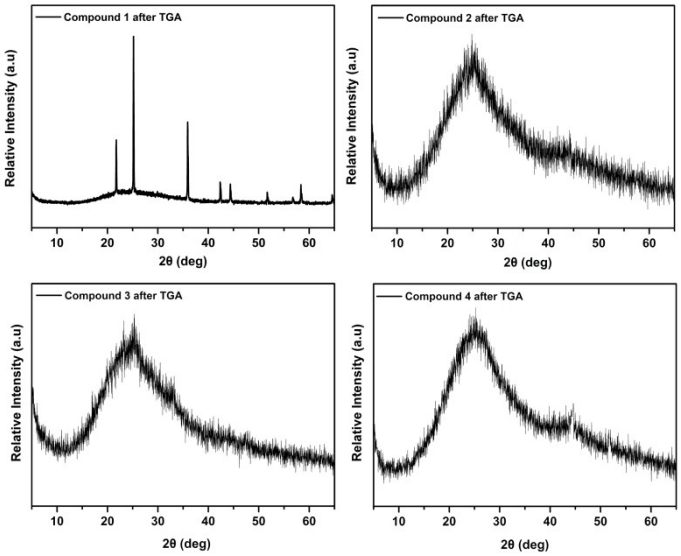

Fig. S16. PXRD patterns of compounds **1**−**4** after TGA study.

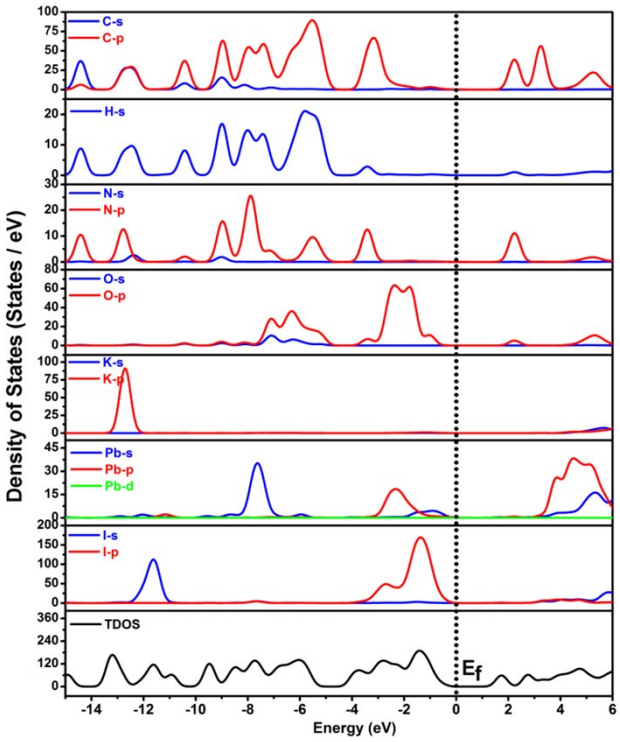

Fig. S17. Total density of states and partial density of states for compound **1**. The Fermi level is set at 0 eV (dotted line).

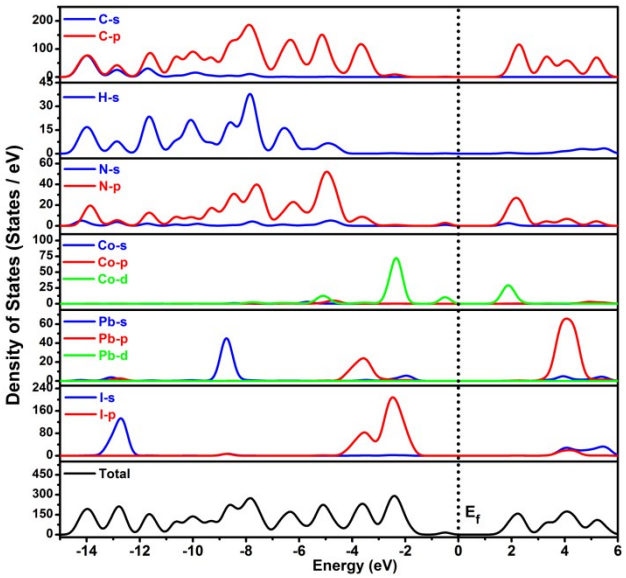

Fig. S18. Total density of states and partial density of states for compound **2**. The Fermi level is set at 0 eV (dotted line).

4. Reference

1. X. B. Chen, H. H. Li, Z. R. Chen, J. B. Liu, J. B. Li, H. J. Dong and Y. L. Wu, *J. Cluster Sci.*, 2009, **20**, 611−620.
2. X. W. Lei, C. Y. Yue, J. C. Wei, R. Q. Li, Y. Li and F. Q. Mi, *Dalton Trans.*, 2016, **45**, 19389−19398.