Hydrogen bonds and steric effects induced structural transition of three layered iodoplumbate hybrids from nonperovskite to perovskite structure

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Supporting Information (SI)

Table. S1 Selected bond lengths (Å) and angles (°) for **1-3**.

Compound **1**			
Pb(1)-I(1)	3.1264(7)	Pb(1)-I(3)	3.1953(5)
Pb(1)-I(3)#1	3.1590(5)	Pb(1)-I(2)#2	3.2692(5)
Pb(1)-I(2)	3.1904(5)	Pb(1)-I(4)	3.3121(7)
I(2)-Pb(1)#3	3.2692(5)	I(3)-Pb(1)#4	3.1590(5)
I(1)-Pb(1)-I(3)#1	93.453(17)	I(3)#1-Pb(1)-I(3)	86.286(6)
I(1)-Pb(1)-I(2)	88.998(16)	I(2)-Pb(1)-I(3)	179.78(2)
I(3)#1-Pb(1)-I(2)	93.570(15)	I(1)-Pb(1)-I(2)#2	91.439(17)
I(1)-Pb(1)-I(3)	91.182(16)	I(3)#1-Pb(1)-I(2)#2	174.848(19)
I(2)-Pb(1)-I(2)#2	84.891(6)	I(2)-Pb(1)-I(4)	92.530(17)
I(3)-Pb(1)-I(2)#2	95.237(14)	I(3)-Pb(1)-I(4)	87.302(17)
I(1)-Pb(1)-I(4)	174.691(16)	I(2)#2-Pb(1)-I(4)	83.638(17)
I(3)#1-Pb(1)-I(4)	91.527(17)		
Pb(1)-I(2)-Pb(1)#3	162.73(2)	Pb(1)#4-I(3)-Pb(1)	167.41(2)
Compound **2**			
Pb(1)-I(2)#1	3.1764(2)	Pb(2)-I(4)	3.0706(3)
Pb(1)-I(2)	3.1764(2)	Pb(2)-I(6)	3.1058(3)
Pb(1)-I(1)#1	3.1802(3)	Pb(2)-I(7)	3.1654(3)
Pb(1)-I(1)	3.1802(3)	Pb(2)-I(1)#2	3.2392(3)
Pb(1)-I(3)	3.2561(3)	Pb(2)-I(2)	3.3207(3)
Pb(1)-I(3)#1	3.2561(3)	Pb(2)-I(5)	3.4759(3)
Pb(3)-I(8)	3.0490(4)	Pb(3)-I(6)	3.2439(3)
Pb(3)-I(9)#3	3.1597(3)	Pb(3)-I(7)	3.3259(3)
Pb(3)-I(9)	3.2128(3)	Pb(3)-I(5)	3.5456(3)
I(2)#1-Pb(1)-I(2)	180.0	I(1)#1-Pb(1)-I(3)	95.222(8)
I(2)#1-Pb(1)-I(1)#1	88.434(7)	I(1)-Pb(1)-I(3)	84.778(8)
I(2)-Pb(1)-I(1)#1	91.566(7)	I(1)#1-Pb(1)-I(3)#1	84.779(7)
I(2)#1-Pb(1)-I(1)	91.566(7)	I(1)-Pb(1)-I(3)#1	95.221(8)
I(2)-Pb(1)-I(1)	88.434(7)	I(1)#1-Pb(1)-I(1)	180.000(1)
I(2)#1-Pb(1)-I(3)	91.173(7)	I(2)#1-Pb(1)-I(3)#1	88.827(7)
I(2)-Pb(1)-I(3)	88.827(7)	I(2)-Pb(1)-I(3)#1	91.173(7)
I(3)-Pb(1)-I(3)#1	180.000(7)	I(4)-Pb(2)-I(6)	96.060(8)

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I(4)-Pb(2)-I(7)	93.647(9)	I(4)-Pb(2)-I(2)	96.189(8)
I(6)-Pb(2)-I(7)	91.393(7)	I(6)-Pb(2)-I(2)	166.209(8)
I(4)-Pb(2)-I(1)#2	93.862(8)	I(7)-Pb(2)-I(2)	94.128(7)
I(6)-Pb(2)-I(1)#2	86.515(7)	I(1)#2-Pb(2)-I(2)	86.362(7)
I(7)-Pb(2)-I(1)#2	172.378(8)	I(4)-Pb(2)-I(5)	174.788(7)
I(6)-Pb(2)-I(5)	87.609(8)	I(1)#2-Pb(2)-I(5)	90.046(8)
I(7)-Pb(2)-I(5)	82.540(8)	I(2)-Pb(2)-I(5)	80.603(7)
I(8)-Pb(3)-I(9)#3	91.614(9)	I(9)#3-Pb(3)-I(7)	174.305(8)
I(8)-Pb(3)-I(9)	97.786(8)	I(9)-Pb(3)-I(7)	88.502(7)
I(9)#3-Pb(3)-I(9)	92.696(7)	I(6)-Pb(3)-I(7)	86.171(7)
I(8)-Pb(3)-I(6)	93.022(8)	I(8)-Pb(3)-I(5)	172.667(8)
I(9)#3-Pb(3)-I(6)	91.616(7)	I(9)#3-Pb(3)-I(5)	95.293(8)
I(9)-Pb(3)-I(6)	168.240(8)	I(9)-Pb(3)-I(5)	84.368(7)
I(8)-Pb(3)-I(7)	93.741(9)	I(6)-Pb(3)-I(5)	84.344(7)
I(7)-Pb(3)-I(5)	79.276(8)		
Pb(1)-I(1)-Pb(2)#4	162.051(8)	Pb(2)-I(6)-Pb(3)	80.416(7)
Pb(1)-I(2)-Pb(2)	160.651(9)	Pb(2)-I(7)-Pb(3)	78.308(7)
Pb(2)-I(5)-Pb(3)	71.454(7)	Pb(3)#3-I(9)-Pb(3)	87.304(7)

Compound 3			
Pb(1)-I(2)	3.1905(5)	Pb(1)-I(1)	3.2282(5)
Pb(1)-I(2)#1	3.1905(5)	Pb(1)-I(3)	3.2327(5)
Pb(1)-I(1)#1	3.2282(5)	Pb(1)-I(3)#1	3.2327(5)
Pb(2)-I(4)	2.9810(6)	Pb(2)-I(2)#1	3.2504(6)
Pb(2)-I(3)	3.1894(6)	Pb(2)-I(2)#3	3.2897(6)
Pb(2)-I(1)#2	3.2341(6)		
I(2)-Pb(1)-I(2)#1	180.0	I(2)-Pb(1)-I(1)#1	90.035(14)
I(2)#1-Pb(1)-I(1)#1	89.965(14)	I(2)#1-Pb(1)-I(1)	90.035(14)
I(2)-Pb(1)-I(1)	89.965(14)	I(1)#1-Pb(1)-I(1)	180.0
I(2)-Pb(1)-I(3)	91.181(13)	I(1)#1-Pb(1)-I(3)	90.673(12)
I(2)#1-Pb(1)-I(3)	88.819(13)	I(1)-Pb(1)-I(3)	89.327(12)
I(2)-Pb(1)-I(3)#1	88.819(13)	I(1)#1-Pb(1)-I(3)#1	89.327(12)
I(2)#1-Pb(1)-I(3)#1	91.181(13)	I(1)-Pb(1)-I(3)#1	90.673(12)
I(3)-Pb(1)-I(3)#1	180.0	I(3)-Pb(2)-I(1)#2	85.609(15)
I(4)-Pb(2)-I(3)	95.622(16)	I(4)-Pb(2)-I(2)#1	90.393(16)
I(4)-Pb(2)-I(1)#2	92.807(15)	I(3)-Pb(2)-I(2)#1	88.528(14)
I(1)#2-Pb(2)-I(2)#1	173.569(16)	I(1)#2-Pb(2)-I(2)#3	98.287(15)
I(4)-Pb(2)-I(2)#3	94.516(16)	I(2)#1-Pb(2)-I(2)#3	87.011(10)
I(3)-Pb(2)-I(2)#3	168.948(14)		
Pb(1)-I(1)-Pb(2)#2	96.584(13)	Pb(1)-I(2)-Pb(2)#4	132.565(17)
Pb(1)-I(2)-Pb(2)#1	91.035(15)	Pb(2)#1-I(2)-Pb(2)#4	135.936(17)
Pb(2)-I(3)-Pb(1)	91.379(13)		

Symmetry code: for 1: #1 -x, -y+1, -z+1; #2 x+1, y, z; #3 -x+1, -y+1, -z; #4 x-1, y, z; for 2: #1 -x+2, -y+1, -z+2; #2 -x+2, -y, -z+2; #3 x, -y+1/2, z-1/2; #4 x, -y+1/2, z+1/2; #5 -x+1, -y, -z+2; for 3: #1 -x+2, -y+1, -z+2 ; #2 -x+2, -y, -z+2; #3 x, -y+1/2, z-1/2; #4 x, -y+1/2, z+1/2; #5 -x+1, -y, -z+2.

Table **S2.** The correlation among crystal color, band gap energy (E_g) and Pb-I-Pb bond angles in the compound **1** and reported perovskite iodoplumbates

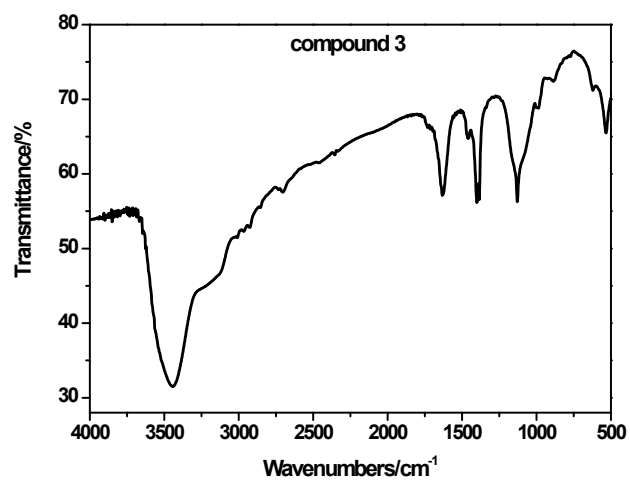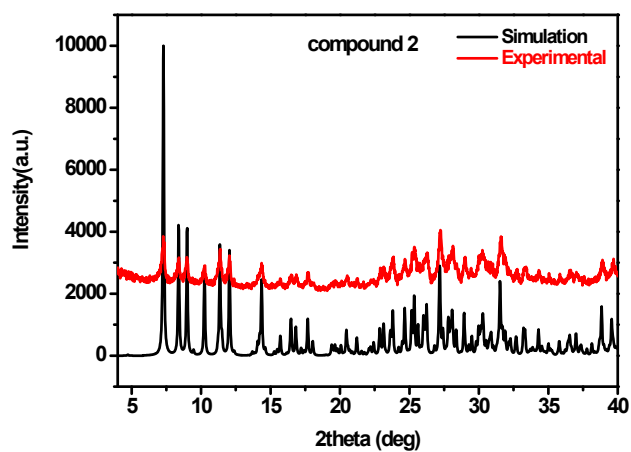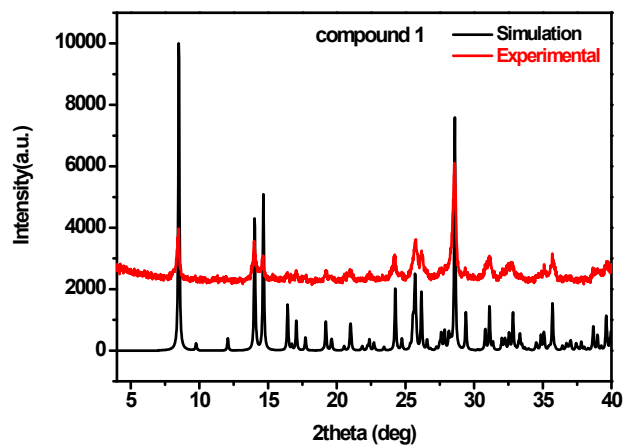| Compound	Crystal color	Pb-I-Pb	Eg(eV)
(CI-(CH$_2$)$_2$-NH$_3$)$_2$PbI$_4$[19a]	red	178.07(3), 176.68(2)	2.2
(Br-(CH$_2$)$_2$-NH$_3$)$_2$PbI$_4$[19a]	red	178.49(3)	2.2
(OH-(CH$_2$)$_3$-NH$_3$)$_2$PbI$_4$[13]	red	163.679(13)	
[H$_2$DMAPA][PbI$_4$](compound1)	red	162.73(2), 167.41(2)	2.21
(OH-(CH$_2$)$_2$-NH$_3$)$_2$PbI$_4$[16a]	orange	159.836(18)	2.31
(I-(CH$_2$)$_2$-NH$_3$)$_2$PbI$_4$[19a]	orange	147.379(15)	2.45
(BAESBT)PbI$_4$[19b]	orange	149.40(3), 151.87(3)	2.535
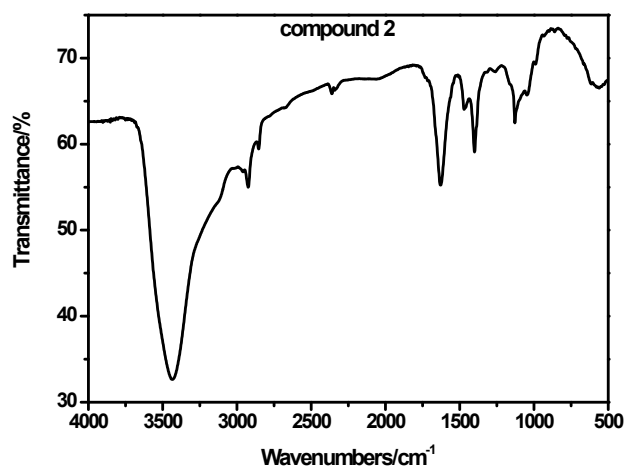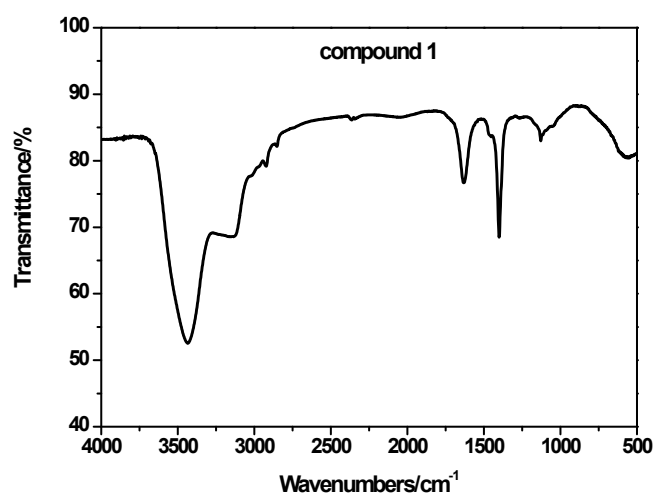
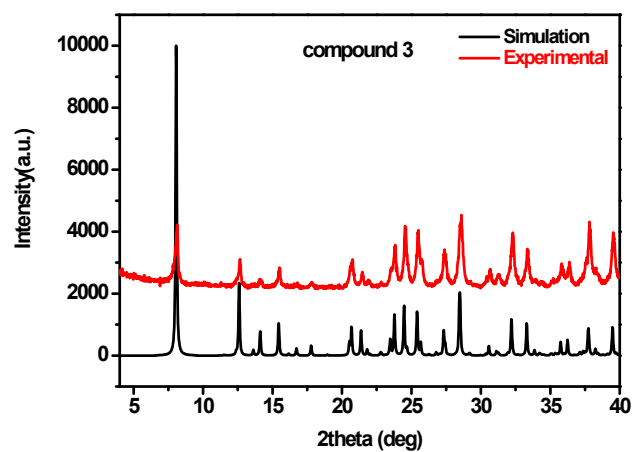**Figure. S1** IR spectra for **1** -3

Fig. S2 Experimental XRPD patterns of compound **1**-**3** exposed in air (red) and simulation patterns of compound **1**

-**3** (black).