Dual-emissions and thermochromic luminescences of isomorphic chiral twofold interpenetrated 3-D nets built from I^1O^2 type hybrid inorganic-organic frameworks of $[NH_2(CH_3)_2]_3[Pb_2X_3(BDC)_2]$ (X = Br, I)

Shao-Xian Liu,[a] Guo-Jun Yuan,[b] Lu Zhai,*[a] Lifeng Wang,[c] Hong-Bin Luo,[a] Xiao-Ming Ren*[a,d,e]

[a] State Key Laboratory of Materials-Oriented Chemical Engineering and College of Chemistry & Molecular Engineering, Nanjing Tech University, Nanjing 210009, P. R. China

[b]School of Environmental Science, Nanjing Xiaozhuang University, Nanjing 211171, P. R. China

[c] Institute for Frontier Materials (IFM), Deakin University, 75 Pigdons Road, Waurn Ponds, Victoria 3216, Australia

[d] College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, P. R. China

[e] State Key Lab & Coordination Chemistry Institute, Nanjing University, Nanjing 210023, P. R. China

Tel.: +86 25 58139476

Fax: +86 25 58139481

Email: zhailu@njtech.edu.cn (LZ); xmren@njtech.edu.cn (XMR)

Contents

Fig. S10 Photographs of **2a/2b** single crystal under (a) visible light at 303 K and ultraviolet with λ = 340-380 nm at (b) 163 K (c) 183 K (d) 203 K (e) 223 K (f) 243 K (g) 263 K (h) 883 K (i) 303 K, which show color of emission alters with temperature change

Table S1: Crystallographic data and refinement parameters for **1b** and **2b**

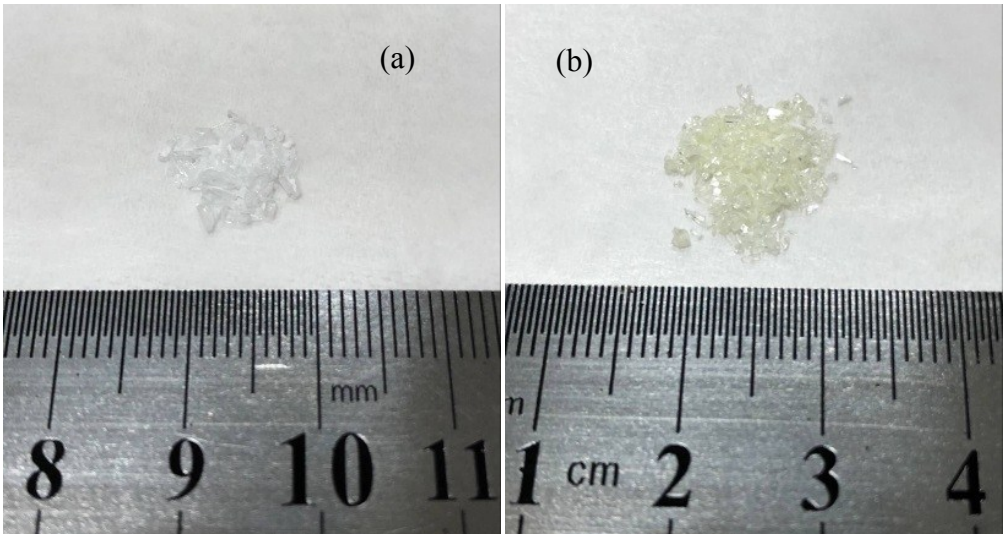

Fig. S1 Photographs of crystals of (a) colorless **1a/1b** (b) light yellow **2a/2b**.

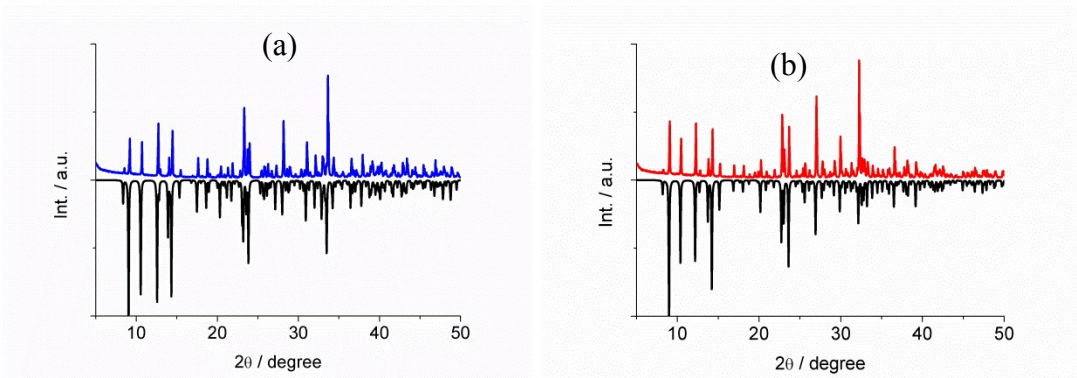

Fig. S2 Experimental and simulated PXRD patters of (a) **1a/1b** and (b) **2a/2b**, respectively. The simulated PXRD patters are obtained from single crystal X-ray diffraction data using Mercury 3.8 program for **1a** and **2a**.

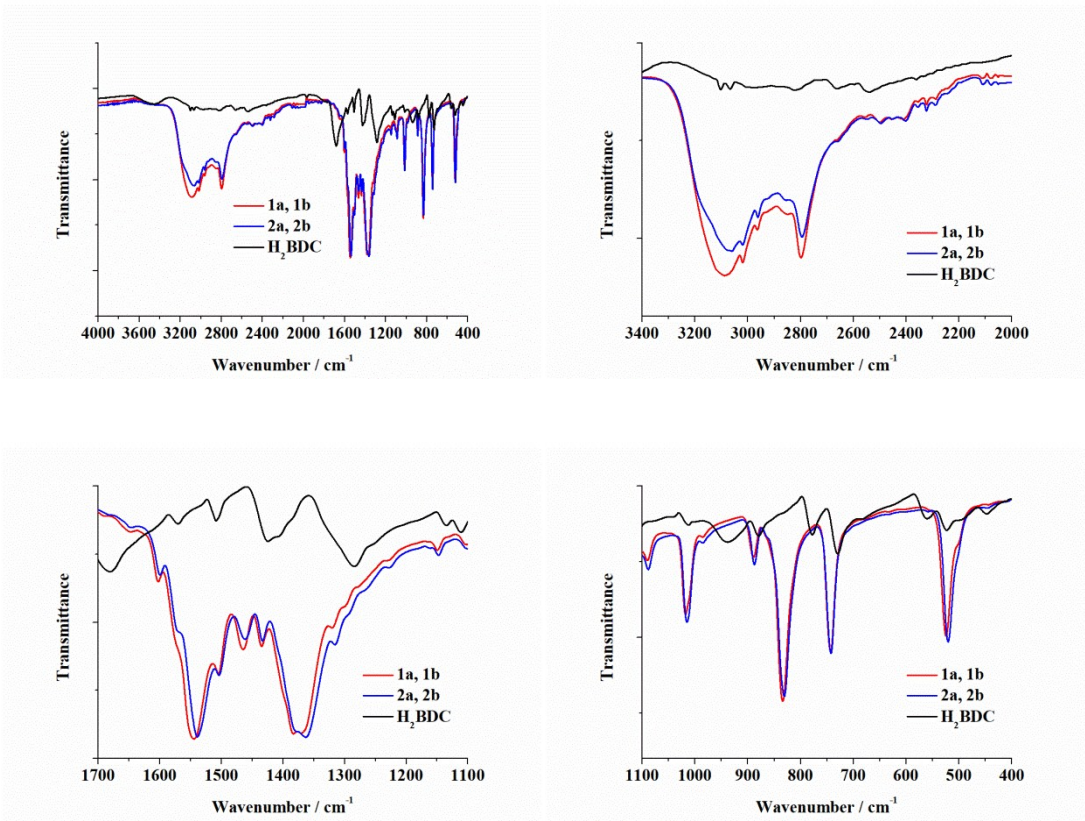

Fig. S3 IR spectra of **1a**/**1b** and **2a**/**2b**, together with the ligand, respectively.

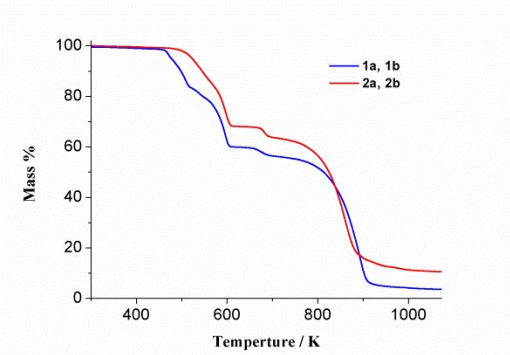

Fig. S4 TG plots of **1a**/**1b** and **2a**/**2b**, showing quite similar thermal behaviors and four steps of losing weight processes in 300-1073 K. The hybrid crystals start to lose weight at ca. 448 K (175 °C) for **1a**/**1b** versus ca. 474 K (201 °C) for **2a**/**2b**.

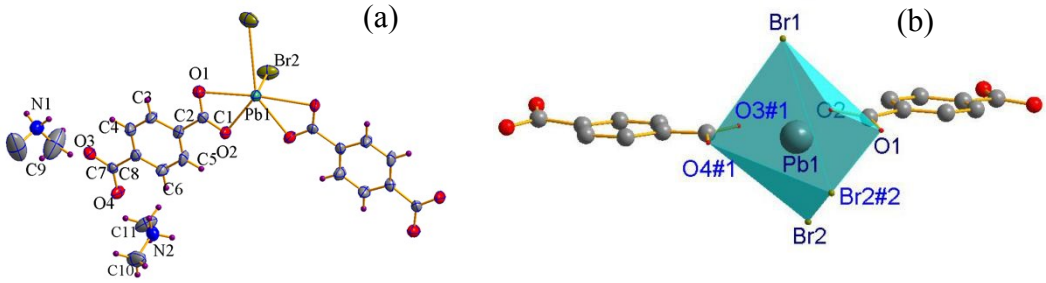

Fig. S5 (a) ORTEP view with the thermal ellipsoid at 50% probability level and (b) coordination pentagonal bipyramidal of $PbBr_3O_4$ in **1b**, where the symmetric codes: #1 = y, -1+x, 1-z; #2 = y, x, 1-z.

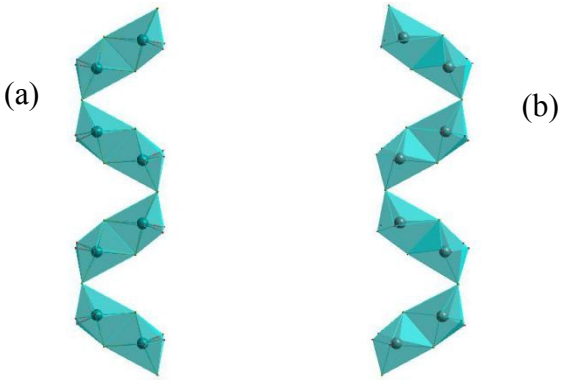

Fig. S6 Helical polyhedral chain in (a) **1a** and (b) **1b**, which are comprised of pentagonal bipyramid dimmers and shows mirror-image relationship, respectively.

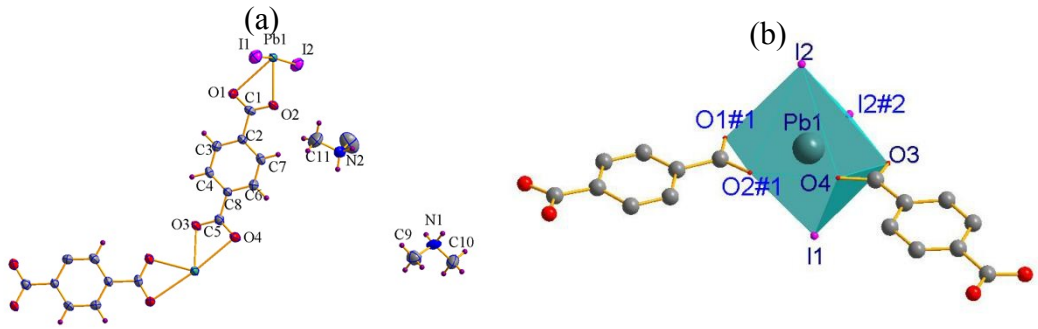

Fig. S7 (a) ORTEP view with the thermal ellipsoid at 50% probability level and (b) coordination pentagonal bipyramidal of PbI_3O_4 in **2a**, where the symmetric codes: #1 = y, 1+x, 1-z; #2 = y, x, 1-z.

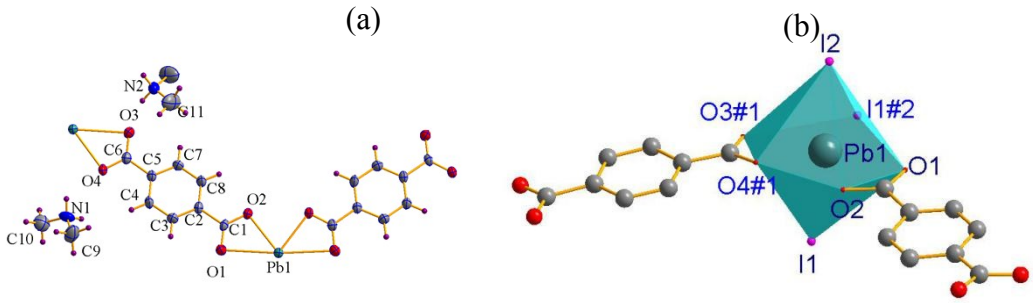

Fig. S8 (a) ORTEP view with the thermal ellipsoid at 50% probability level and (b) coordination pentagonal bipyramidal of PbI_3O_4 in **2b**, where the symmetric codes: #1 = 2-y, 1-x, 0.5-z; #2 = 1-y, 1-x, 0.5-z.

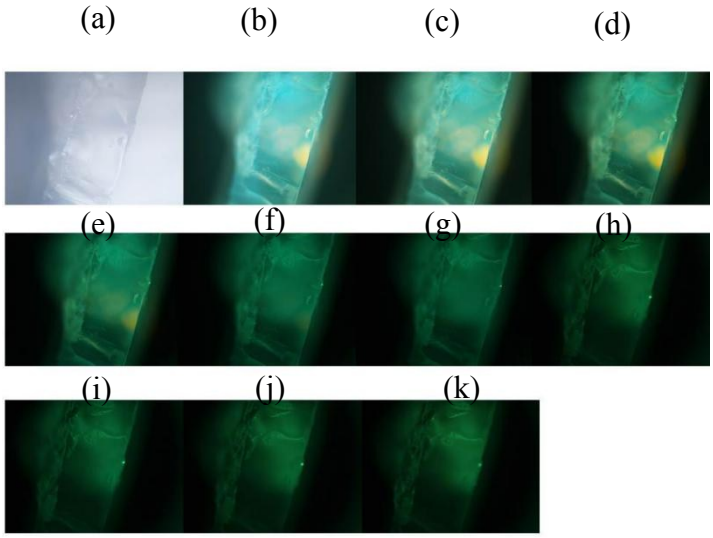

Fig. S9 Photographs of **1a/1b** single crystal under (a) visible light at 303 K and ultraviolet with λ = 340-380 nm at (b) 123 K (c) 143 K (d) 163 K (e) 183 K (f) 203 K (g) 223 K (h) 243 K (i) 263 K (j) 283 K (k) 303 K, which show color of emission alters with temperature change.

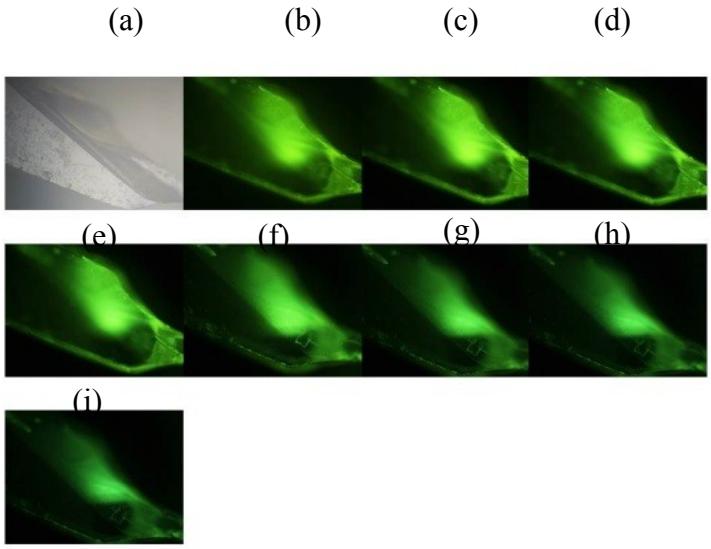

Fig. S10 Photographs of **2a/2b** single crystal under (a) visible light at 303 K and ultraviolet with λ = 340-380 nm at (b) 163 K (c) 183 K (d) 203 K (e) 223 K (f) 243 K (g) 263 K (h) 883 K (i) 303 K, which show color of emission alters with temperature change.

Table S1: Crystallographic data and refinement parameters for **1b** and **2b**

Compound	**1b**	**2b**
Temperature/K	295	278
Chemical formula	$C_{22}H_{32}Br_3N_3O_8Pb_2$	$C_{22}H_{32}I_3N_3O_8Pb_2$
Formula weight	1120.61	1261.59
Wavelength (Å)	0.71073	0.71073
Crystal system	Tetragonal	Tetragonal
Space group	$P4_12_12$	$P4_12_12$
a (Å)	13.8177(5)	13.9190(10)
b (Å)	13.8177(5)	13.9190(10)
c (Å)	16.3601(11)	17.003(3)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V(Å^3) / Z	3123.6(3)/4	3294.1(7)/4
ρ (g·cm^{-3})	2.383	2.544
F(000)	2071	2288
Abs. coeff. (mm^{-1})	14.649	13.063
Flack parameter	0.012(5)	0.022(5)
θ Ranges of data collection (°)	2.894-25.025	2.927-27.558
	$-16 \leq h \leq 16$	$-18 \leq h \leq 18$
Index range	$-16 \leq k \leq 16$	$-18 \leq k \leq 18$
	$-19 \leq l \leq 19$	$-22 \leq l \leq 22$
R_{int}	0.0495	0.0413
Independent reflections /restraints/parameters	2760/0/176	3771/0/177
Refine method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	1.012	1.105

R_1, wR_2 [I>2σ(I)]	R_1 = 0.0269 wR_2 = 0.0500	R_1 = 0.0171 wR_2= 0.0364
R_1, wR_2 [all data]	R_1 = 0.0336 wR_2 = 0.0517	R_1 = 0.0193 wR_2= 0.0369
Residual ($e \cdot Å^{-3}$)	1.794/-0.525	0.503/-0.540

$R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$, $wR_2 = \Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w\ (|F_o|^2)^2]^{1/2}$