Supporting Information

Inserting protonated phenanthroline derivatives to interchain voids of anionic halometallate units to generate hybrid materials with tunable photochromic performance

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Instruments used in this work.

Elemental analyses (C, H, and N) were measured on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). IR spectra were measured on a MAGNA-560 (Nicolet) FT-IR spectrometer with KBr pellets. The luminescence data were measured on an F-7000 FL spectrophotometer. The solid-state UV-Vis spectra were measured on a PerkinElmer Lamda-950 spectrophotometer. Electron paramagnetic resonance (EPR) spectroscopy was measured on a JEOL JES-FA200 EPR spectrometer. The Xe-lamp for photochromic characterization is a Perfect Light PLS-SXE 300. The experimental powder X-ray diffraction (PXRD) analyses were conducted on a Rigaku D/max-2550 diffractometer with Cu-K_α radiation (λ = 1.5418 Å). Simulation of the PXRD curve was carried out by the single-crystal data and diffraction-crystal module of the Mercury software.

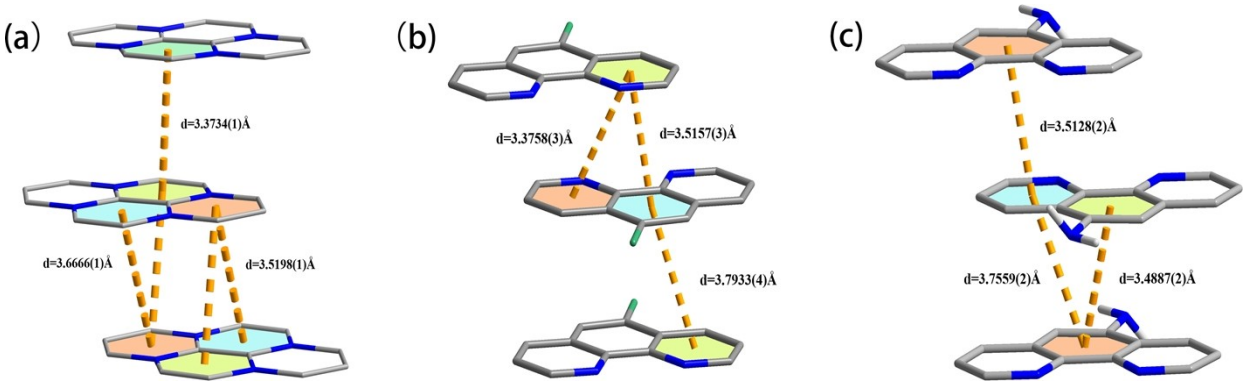

Fig. S1 The π···π stacking interactions for complexes **1**-**3**.

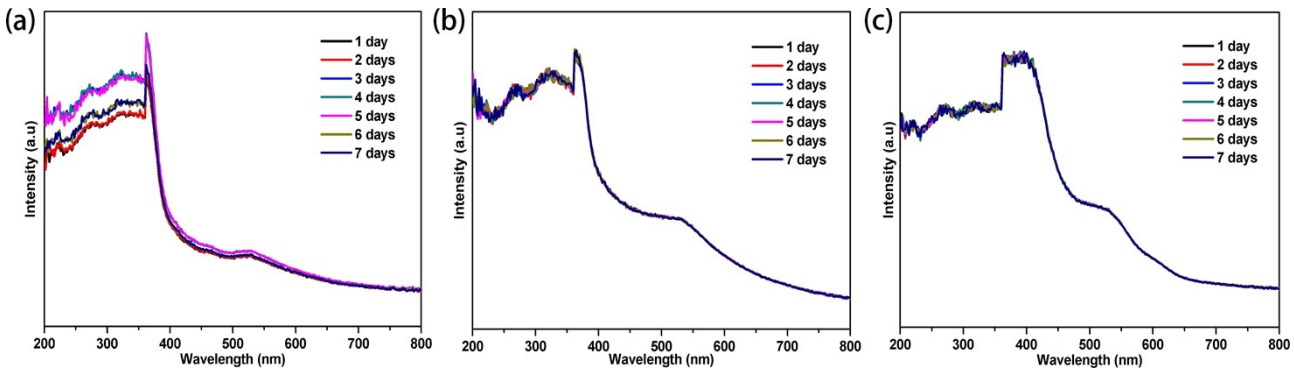

Fig. S2 The time-dependent UV-Vis spectra of **1** (a), **2** (b) and **3** (c).

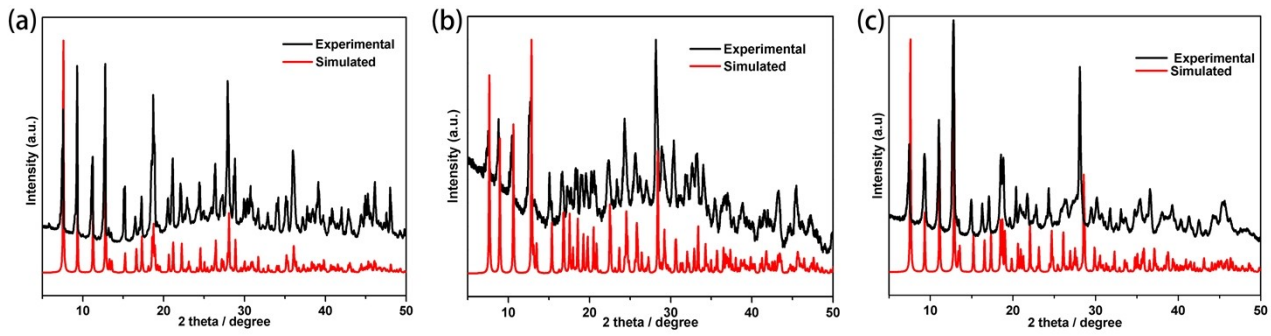

Fig. S3 PXRD patterns of **1** (a), **2** (b) and **3** (c).

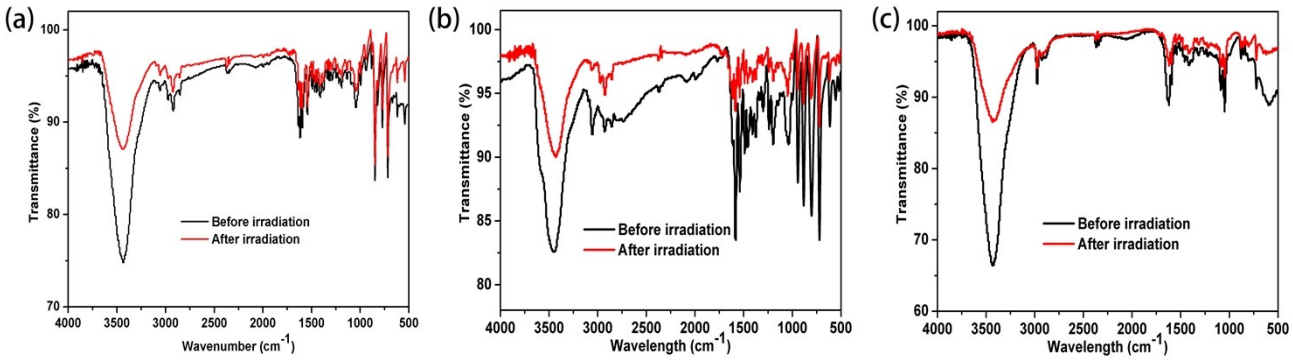

Fig. S4 IR patterns of **1** (a), **2** (b) and **3** (c).

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

Bi(1)-Cl(1)	2.6957(18)	Bi(1)-Cl(3)	2.7523(19)
Bi(1)-Cl(1)#1	2.9718(19)	Bi(1)-Cl(3)#2	2.9249(19)
Bi(1)-Cl(2)	2.5655(19)	Bi(1)-Cl(4)	2.5066(19)
Cl(1)-Bi(1)-Cl(1)#1	83.95(5)	Cl(3)-Bi(1)-Cl(3)#2	83.03(5)
Cl(1)-Bi(1)-Cl(3)#2	93.57(5)	Cl(4)-Bi(1)-Cl(1)#1	171.30(6)
Cl(1)-Bi(1)-Cl(3)	176.21(5)	Cl(4)-Bi(1)-Cl(1)	89.14(6)
Cl(2)-Bi(1)-Cl(1)	93.55(6)	Cl(4)-Bi(1)-Cl(2)	94.92(6)
Cl(2)-Bi(1)-Cl(1)#1	90.80(6)	Cl(4)-Bi(1)-Cl(3)#2	90.48(6)
Cl(2)-Bi(1)-Cl(3)	89.69(6)	Cl(4)-Bi(1)-Cl(3)	92.55(6)
Cl(2)-Bi(1)-Cl(3)#2	171.12(6)	Bi(1)-Cl(1)-Bi(1)#1	96.05(5)
Cl(3)-Bi(1)-Cl(1)#1	94.03(5)	Bi(1)-Cl(3)-Bi(1)#2	96.97(5)
Cl(3)#2-Bi(1)-Cl(1)#1	84.68(6)		

Symmetry code: #1: -x+1, -y+1, -z+1.

Table S2. Selected bond lengths (Å) and angles (°) for **2**

Bi(1)-Cl(2)	2.512(4)	Bi(1)-Cl(3)	2.739(3)
Bi(1)-Cl(4)	2.521(4)	Bi(1)-Cl(1)	2.957(4)
Bi(1)-Cl(1)#1	2.714(3)	Bi(1)-Cl(3)#2	2.961(4)
Cl(2)-Bi(1)-Cl(4)	93.44(17)	Cl(1)#1-Bi(1)-Cl(1)	82.70(11)
Cl(2)-Bi(1)-Cl(1)#1	93.19(14)	Cl(3)-Bi(1)-Cl(1)	92.54(12)
Cl(4)-Bi(1)-Cl(1)#1	90.86(14)	Cl(2)-Bi(1)-Cl(3)#2	168.92(13)
Cl(2)-Bi(1)-Cl(3)	90.15(14)	Cl(4)-Bi(1)-Cl(3)#2	93.69(15)
Cl(4)-Bi(1)-Cl(3)	93.84(14)	Cl(1)#1-Bi(1)-Cl(3)#2	95.17(12)
Cl(1)#1-Bi(1)-Cl(3)	174.06(13)	Cl(3)-Bi(1)-Cl(3)#2	80.93(11)
Cl(2)-Bi(1)-Cl(1)	87.65(15)	Cl(1)-Bi(1)-Cl(3)#2	86.21(13)
Cl(4)-Bi(1)-Cl(1)	173.53(12)		

Symmetry code: #1: -x+2, -y+1, -z.

Table S3. Selected bond lengths (Å) and angles (°) for **3**

Bi(00)-Cl(00)	2.687(2)	Bi(00)-Cl(2)	2.517(3)
Bi(00)-Cl(00)#1	2.983(3)	Bi(00)-Cl(3)	2.518(3)
Bi(00)-Cl(1)#2	2.951(3)	Cl(00)-Bi(00)#1	2.983(3)
Bi(00)-Cl(1)	2.753(3)	Cl(1)-Bi(00)#2	2.951(3)
Cl(00)-Bi(00)-Cl(00)#1	84.27(9)	Cl(2)-Bi(00)-Cl(1)#2	92.89(9)
Cl(00)-Bi(00)-Cl(1)#2	93.75(8)	Cl(2)-Bi(00)-Cl(3)	93.24(12)
Cl(00)-Bi(00)-Cl(1)	175.66(8)	Cl(3)-Bi(00)-Cl(00)#1	86.49(11)
Cl(1)-Bi(00)-Cl(00)#1	93.07(8)	Cl(3)-Bi(00)-Cl(00)	93.02(10)
Cl(1)#2-Bi(00)-Cl(00)#1	88.10(8)	Cl(3)-Bi(00)-Cl(1)	90.23(10)
Cl(1)-Bi(00)-Cl(1)#2	82.72(8)	Cl(3)-Bi(00)-Cl(1)#2	170.87(10)
Cl(2)-Bi(00)-Cl(00)	89.90(10)	Bi(00)-Cl(00)-Bi(00)#1	95.72(9)
Cl(2)-Bi(00)-Cl(00)#1	174.14(8)	Bi(00)-Cl(1)-Bi(00)#2	97.28(8)
Cl(2)-Bi(00)-Cl(1)	92.79(10)		

Symmetry code: #1: -x+1, -y, -z+2.

Table S4. Details of selected hydrogen bond in **1**

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (deg)
C2-H2A···Cl3	0.93	2.923	3.790	155
C3-H3···Cl4	0.93	2.887	3.559	130
C4-H4B···Cl4	0.93	3.146	3.409	102
C9-H9A···Cl4	0.93	2.933	3.564	126
C9-H9A···Cl2	0.93	2.926	3.784	154
C10-H10···Cl4	0.93	2.923	3.574	125

Table S5. Details of selected hydrogen bond in **2**

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (deg)
C1-H1···Cl1	0.93	2.822	3.522	132
C3-H3···Cl1	0.93	3.006	3.430	109
C11-H11···Cl3	0.93	2.861	3.774	167

Table S6. Details of selected hydrogen bond in **3**

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (deg)
N3-H3A···Cl3	0.94	2.80	3.1811(3)	105
C8-H8···Cl1	0.95	2.76	3.6827(3)	164