Supporting Information

X-ray scintillation and photoluminescence of isomorphic ionic bismuth halides with $[Amim]^+$ or $[Ammim]^+$ cation

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Table S1 Crystallographic data for compound **1**, **2** and **3**.

Compound	**1**	**2**	**3**
Empirical formula	$BiBr_4C_{18}H_{21}N_4O_2$	$BiCl_4C_{18}H_{21}N_4O_2$	$BiCl_4C_{17}H_{19}N_4O_2$
Formula Mass	854.01	676.17	662.14
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Pca2_1$	$Pca2_1$	$Pca2_1$
a/Å	15.1759(16)	14.9967(16)	14.6337(9)
b/Å	9.7830(12)	9.4857(12)	9.4088(5)
c/Å	16.7444(17)	16.3613(17)	16.1330(8)
V/Å^3	2486.0(5)	2327.5(5)	2221.3(2)
Z	4	4	4
T/K	295(2)	295(2)	300(2)
λ/Å	0.71073	0.71073	0.71073
F(000)	1584	1296	1264
ρ_{calcd}/g cm^{-3}	2.282	1.930	1.980
μ/mm^{-1}	13.542	8.056	8.439
Measured refls.	45407	13952	15732
Independent refls.	5632	5504	5089
No. of parameters	265	265	256
R_{int}	0.1086	0.0480	0.0392
R_1 ($I > 2\sigma(I)$)[a]	0.0411	0.0391	0.0249
$wR(F^2)$ ($I > 2\sigma(I)$)[b]	0.0915	0.0716	0.0483
GOF	1.074	1.002	0.990
CCDC number	2092480	2092481	2092482

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

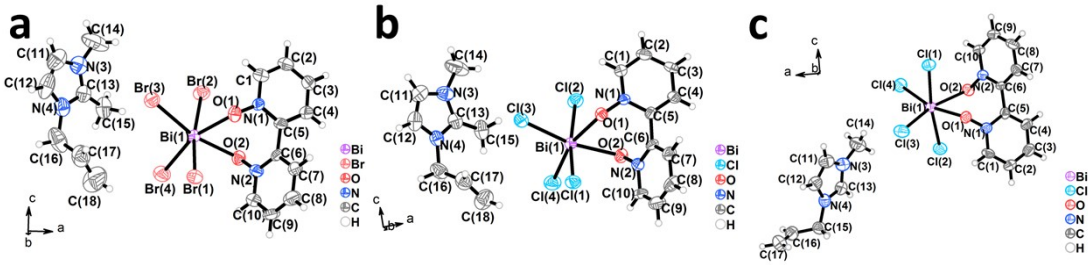

Fig. S1 *ORTEP* drawings (50% ellipsoid probability) of the asymmetric units of **1** (a), **2** (b) and **3** (c).

Table S2 Selected bond lengths (Å) and bond angles (°) for **1**, **2** and **3**.

1		**2**		**3**	
Bi(1)−O(1)	2.445(10)	Bi(1)−O(1)	2.437(7)	Bi(1)−O(1)	2.390(5)
Bi(1)−O(2)	2.413(10)	Bi(1)−O(2)	2.434(8)	Bi(1)−O(2)	2.417(5)
Bi(1)−Br(1)	2.8434(16)	Bi(1)−Cl(1)	2.695(3)	Bi(1)−Cl(1)	2.663(2)
Bi(1)−Br(2)	2.8211(17)	Bi(1)−Cl(2)	2.682(3)	Bi(1)−Cl(2)	2.683(2)
Bi(1)−Br(3)	2.8581(16)	Bi(1)−Cl(3)	2.689(3)	Bi(1)−Cl(3)	2.660(2)
Bi(1)−Br(4)	2.8050(16)	Bi(1)−Cl(4)	2.639(3)	Bi(1)−Cl(4)	2.727(2)
O(1)−N(1)	1.322(14)	O(1)−N(1)	1.324(11)	O(1)−N(1)	1.335(7)
O(2)−N(2)	1.342(15)	O(2)−N(2)	1.337(12)	O(2)−N(2)	1.339(7)
O(2)−Bi(1)−O(1)	73.5(3)	O(2)−Bi(1)−O(1)	73.2(2)	O(1)−Bi(1)−O(2)	73.73(14)
O(1)−Bi(1)−Br(1)	82.4(2)	O(1)−Bi(1)−Cl(1)	82.26(18)	O(1)−Bi(1)−Cl(1)	83.87(12)
O(1)−Bi(1)−Br(2)	89.1(2)	O(1)−Bi(1)−Cl(2)	88.44(19)	O(1)−Bi(1)−Cl(2)	90.00(13)
O(1)−Bi(1)−Br(3)	91.3(2)	O(1)−Bi(1)−Cl(3)	92.22(18)	O(1)−Bi(1)−Cl(3)	87.53(12)
O(1)−Bi(1)−Br(4)	161.3(2)	O(1)−Bi(1)−Cl(4)	162.51(19)	O(1)−Bi(1)−Cl(4)	164.06(13)
O(2)−Bi(1)−Br(1)	89.8(2)	O(2)−Bi(1)−Cl(1)	89.02(19)	O(2)−Bi(1)−Cl(1)	88.20(13)
O(2)−Bi(1)−Br(2)	85.6(2)	O(2)−Bi(1)−Cl(2)	85.91(19)	O(2)−Bi(1)−Cl(2)	85.34(12)
O(2)−Bi(1)−Br(3)	164.5(2)	O(2)−Bi(1)−Cl(3)	165.34(19)	O(2)−Bi(1)−Cl(3)	161.22(13)
O(2)−Bi(1)−Br(4)	88.2(2)	O(2)−Bi(1)−Cl(4)	89.6(2)	O(2)−Bi(1)−Cl(4)	91.48(12)
Br(2)−Bi(1)−Br(1)	171.18(5)	Cl(2)−Bi(1)−Cl(1)	170.38(9)	Cl(1)−Bi(1)−Cl(2)	172.13(5)
Br(4)−Bi(1)−Br(1)	94.40(5)	Cl(4)−Bi(1)−Cl(1)	94.91(11)	Cl(1)−Bi(1)−Cl(4)	89.88(8)
Br(4)−Bi(1)−Br(2)	92.92(5)	Cl(4)−Bi(1)−Cl(2)	93.22(10)	Cl(2)−Bi(1)−Cl(4)	94.76(6)
Br(1)−Bi(1)−Br(3)	90.74(5)	Cl(3)−Bi(1)−Cl(1)	90.45(9)	Cl(3)−Bi(1)−Cl(1)	91.09(6)
Br(2)−Bi(1)−Br(3)	91.78(5)	Cl(2)−Bi(1)−Cl(3)	92.39(10)	Cl(3)−Bi(1)−Cl(2)	93.59(9)
Br(4)−Bi(1)−Br(3)	107.21(6)	Cl(4)−Bi(1)−Cl(3)	105.09(10)	Cl(3)−Bi(1)−Cl(4)	107.29(6)
N(1)−O(1)−Bi(1)	119.5(7)	N(1)−O(1)−Bi(1)	120.3(7)	N(1)−O(1)−Bi(1)	118.5(4)
N(2)−O(2)−Bi(1)	115.9(7)	N(2)−O(2)−Bi(1)	115.7(7)	N(2)−O(2)−Bi(1)	116.0(4)
O(1)−N(1)−C(1)	119.5(12)	O(1)−N(1)−C(1)	119.9(9)	O(1)−N(1)−C(1)	119.2(6)
O(1)−N(1)−C(5)	119.3(12)	O(1)−N(1)−C(5)	119.2(10)	O(1)−N(1)−C(5)	119.4(8)
O(2)−N(2)−C(10)	118.7(12)	O(2)−N(2)−C(10)	119.3(10)	O(2)−N(2)−C(10)	118.9(6)
C(6)−N(2)−O(2)	120.5(12)	O(2)−N(2)−C(6)	120.4(10)	O(2)−N(2)−C(6)	119.3(8)
C(1)−N(1)−C(5)	120.9(13)	C(1)−N(1)−C(5)	120.8(11)	C(1)−N(1)−C(5)	121.3(9)
C(6)−N(2)−C(10)	120.8(13)	C(6)−N(2)−C(10)	120.3(11)	C(10)−N(2)−C(6)	121.7(8)
C(17)−C(16)−N(4)	115(2)	C(17)−C(16)−N(4)	113.1(13)	N(4)−C(15)−C(16)	112.4(7)

Table S3 Hydrogen bonding data for **1**, **2** and **3**.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<(DHA) (°)
1				
C(1)−H(1)···Br(1)#1	0.93	3.10	3.691(16)	122.7
C(2)−H(2)···Br(1)#1	0.93	3.02	3.642(18)	125.4
C(4)−H(4)···Br(4)#2	0.93	3.12	3.835(15)	135.1
C(7)−H(7)···Br(1)#3	0.93	3.04	3.723(14)	131.4

C(7)−H(7)···Br(3)#3	0.93	3.06	3.838(15)	142.1
C(9)−H(9)···Br(2)#4	0.93	3.07	3.675(16)	124.2
C(9)−H(9)···Br(3)#4	0.93	2.92	3.740(16)	147.5
C(10)−H(10)···Br(2)#4	0.93	3.08	3.685(17)	124.0
C(12)−H(12)···Br(3)#5	0.93	2.86	3.773(18)	168.7
C(15)−H(15B)···O(2)#6	0.96	2.50	3.41(2)	157.1
C(15)−H(15C)···Br(3)	0.96	2.86	3.661(17)	141.0

Symmetry transformations used to generate equivalent atoms:
#1 -*x*+3/2, *y*, *z*+1/2; #2 *x*+1/2, -*y*+1, *z*; #3 *x*+1/2, -*y*, *z*; #4 -*x*+3/2, *y*, *z*-1/2; #5 *x*-1/2, -*y*, *z*; #6 *x*-1/2, -*y*+1, *z*.

2

C(1)−H(1)···Cl(1)#1	0.93	2.97	3.556(13)	122.4
C(2)−H(2)···Cl(1)#1	0.93	2.89	3.520(15)	125.9
C(4)−H(4)···Cl(4)#2	0.93	2.94	3.668(12)	136.1
C(7)−H(7)···Cl(1)#3	0.93	2.97	3.645(12)	130.7
C(7)−H(7)···Cl(3)#3	0.93	2.89	3.683(13)	143.4
C(9)−H(9)···Cl(3)#4	0.93	2.76	3.612(16)	153.2
C(10)−H(10)···Cl(2)#4	0.93	2.90	3.538(13)	126.8
C(12)−H(12)···Cl(3)#5	0.93	2.69	3.623(14)	176.4
C(15)−H(15C)···Cl(3)	0.96	2.90	3.617(13)	132.3

Symmetry transformations used to generate equivalent atoms:
#1 -*x*+3/2, *y*, *z*+1/2; #2 *x*+1/2, -*y*+1, *z*; #3 *x*+1/2, -*y*, *z*; #4 -*x*+3/2, *y*, *z*-1/2; #5 *x*-1/2, -*y*, *z*.

3

C(1)−H(1)···Cl(1)#1	0.93	2.79	3.487(7)	132.3
C(4)−H(4)···Cl(4)#2	0.93	2.98	3.639(8)	129.4
C(7)−H(7)···Cl(1)#3	0.93	2.98	3.657(7)	130.4
C(7)−H(7)···Cl(3)#3	0.93	2.89	3.633(8)	138.2
C(9)−H(9)···Cl(3)#4	0.93	2.76	3.603(15)	150.9
C(10)−H(10)···Cl(2)#4	0.93	2.78	3.488(8)	133.8
C(11)−H(11)···O(1)#5	0.93	2.59	3.379(9)	142.5
C(13)−H(13)···Cl(4)#6	0.93	2.89	3.679(8)	143.3
C(14)−H(14A)···Cl(3)	0.96	2.95	3.737(9)	139.8
C(14)−H(14B)···O(2)#7	0.96	2.65	3.578(10)	161.7
C(15)−H(15A)···Cl(1)#8	0.97	2.87	3.626(8)	136.0
C(15)−H(15B)···Cl(4)#6	0.97	2.88	3.746(8)	149.7

Symmetry transformations used to generate equivalent atoms:
#1 -*x*+1/2, *y*, *z*-1/2; #2 *x*-1/2, -*y*, *z*; #3 *x*-1/2, -*y*+1, *z*; #4 –*x*+1/2, *y* , *z*+1/2; #5 *x*+1/2, -*y*+1, *z*; #6 -*x*+1, -*y*, *z*-1/2; #7 *x*+1/2, -*y*, *z*; #8 –*x*+1, -*y*+1, *z*-1/2.

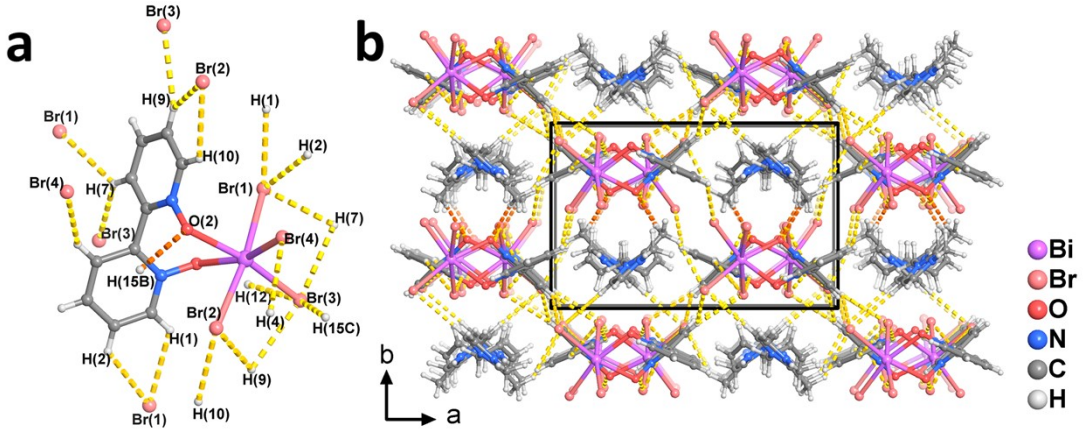

Fig. S2 (a) Hydrogen bond environments for **1**. (b) 3D supramolecular packing structure of **1** along the *c* axis. The C–H···*X* hydrogen bond is presented in yellow dotted line; while the C–H···O hydrogen bond is presented in orange dotted line.

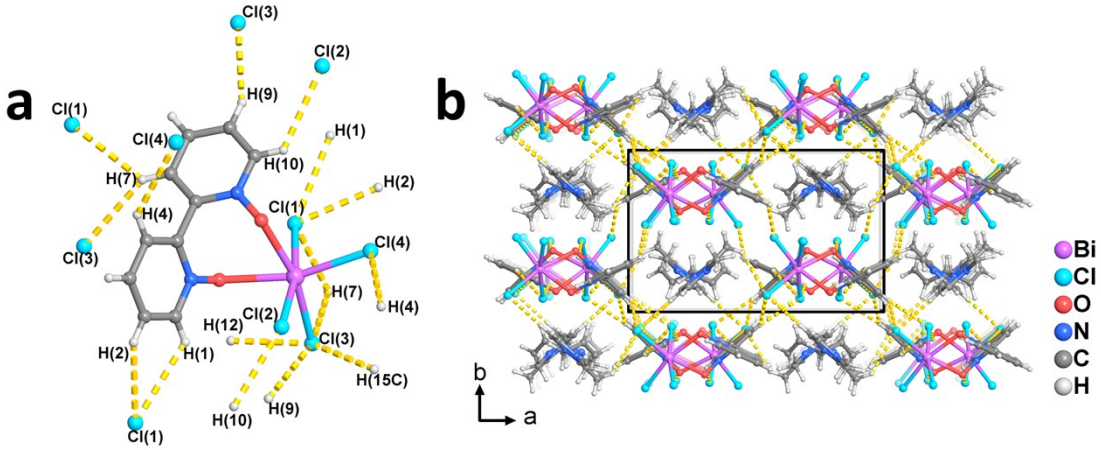

Fig. S3 (a) Hydrogen bond environments for **2**. (b) 3D supramolecular packing structure of **2** along the *c* axis. The C–H···*X* hydrogen bond is presented in yellow dotted line.

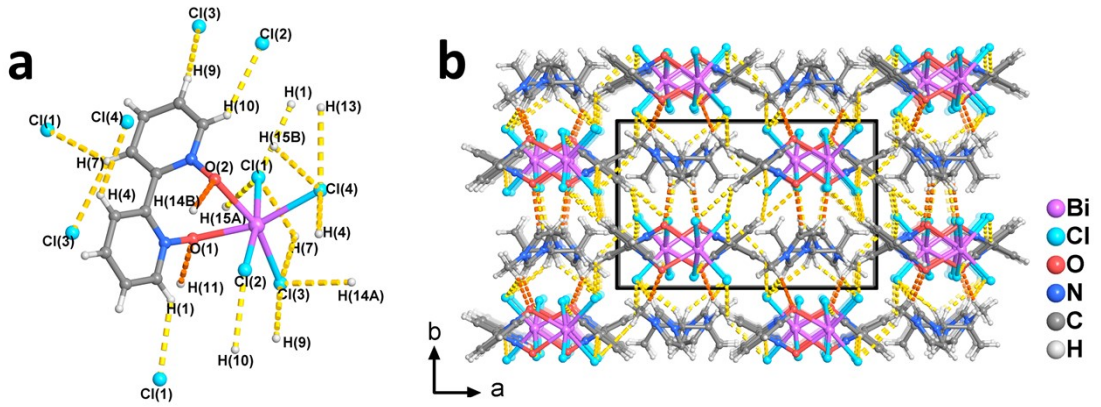

Fig. S4 (a) Hydrogen bond environments for **3**. (b) 3D supramolecular packing structure of **3** along the *c* axis. The C–H···*X* hydrogen bond is presented in yellow dotted line; while the C–H···O hydrogen bond is presented in orange dotted line.

Table S4 Selected anion−π interaction data for **1**.

Y−X(I)···Cg(J)	ARU(J)	X···Cg(Å)	<Y−X···Cg(°)	Y···Cg(Å)	Y−X, Pi
Bi(1)−Br(1)→Cg(2)	1555	3.810(7)	80.00(10)	4.341(7)	24.09
Bi(1)−Br(2)→Cg(3)	4565	3.602(8)	126.07(16)	5.736(8)	24.13
Bi(1)−Br(3)→Cg(1)	4455	3.812(6)	151.16(11)	6.464(6)	50.34

Cg(1): N(1)→C(1)→C(2)→C(3)→C(4)→C(5); Cg(2): N(2)→C(6)→C(7)→C(8)→C(9)→C(10); Cg(3): N(3)→C(11)→C(12)→N(4)→C(13). [1555] = *x*, *y*, *z*; [4455] = -1/2+*x*, -*y*, *z*; [4565] = 1/2+*x*, 1-*y*, *z*.

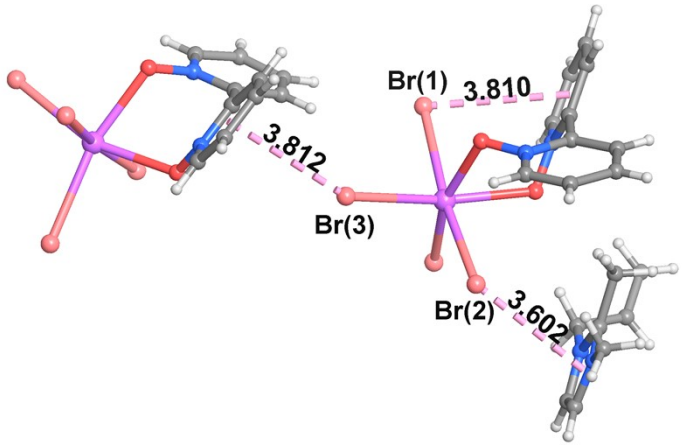

Fig. S5 The view of anion···π interaction (pink dotted line) for **1**.

Table S5 Selected anion−π interaction data for **2**.

Y−X(I)···Cg(J)	ARU(J)	X···Cg(Å)	<Y−X···Cg(°)	Y···Cg(Å)	Y−X, Pi
Bi(1)−Cl(2)→Cg(3)	4565	3.561(7)	130.07(15)	5.672(6)	25.31
Bi(1)−Cl(3)→Cg(1)	4455	3.824(6)	153.41(13)	6.344(5)	51.60

Cg(1): N(1)→C(1)→C(2)→C(3)→C(4)→C(5); Cg(3): N(3)→C(11)→C(12)→N(4)→C(13). [4455] = -1/2+*x*, -*y*, *z*; [4565] = 1/2+*x*, 1-*y*, *z*.

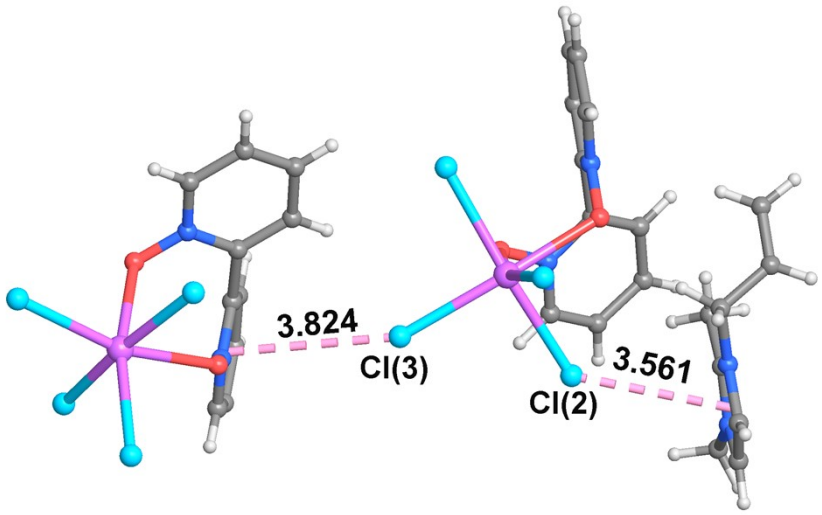

Fig. S6 The view of anion−π interactions (pink dotted line) for **2**.

Table S6 Selected anion−π interaction data for **3**.

Y−X(I)···Cg(J)	ARU(J)	X···Cg(Å)	<Y−X···Cg(°)	Y···Cg(Å)	Y−X, Pi
Bi(1)−Cl(2)→Cg(3)	4455	3.550(4)	143.29(9)	5.922(4)	42.42
Bi(1)−Cl(3)→Cg(1)	4565	3.639(4)	162.50(10)	6.228(4)	57.98
Bi(1)−Cl(4)→Cg(2)	4555	3.742(4)	160.83(10)	6.380(4)	56.22

Cg(1): N(1)→C(1)→C(2)→C(3)→C(4)→C(5); Cg(2): N(2)→C(6)→C(7)→C(8)→C(9)→C(10); Cg(3): N(3)→C(11)→C(12)→N(4)→C(13). [4455] = -1/2+*x*, -*y*, *z*; [4565] = 1/2+*x*, 1-*y*, *z*; [4555] = 1/2+*x*, -*y*, *z*.

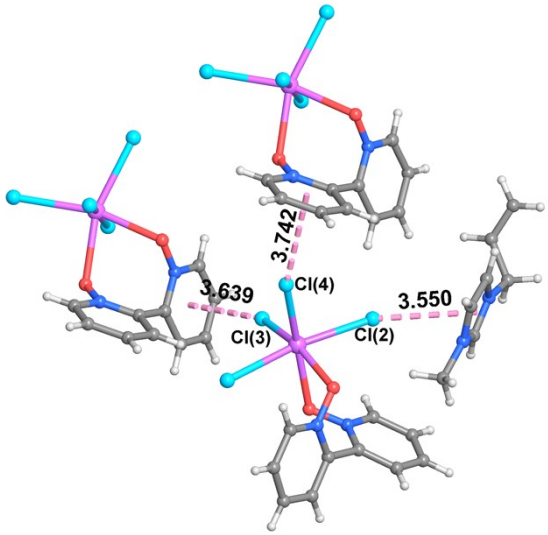

Fig. S7 The view of anion−π interactions (pink dotted line) for **3**.

Table S7 Selected C−H−π interaction data for **1**.

X−H(I)···Cg(J)	ARU(J)	H···Cg(Å)	<X−H···Cg(°)	X···Cg(Å)	X−H, Pi
C(15)−H(15A)→Cg(1)	4465	2.85	134	3.584(17)	46.00

Cg(1): N(1)→C(1)→C(2)→C(3)→C(4)→C(5). [4465] = -1/2+*x*, 1-*y*, *z*.

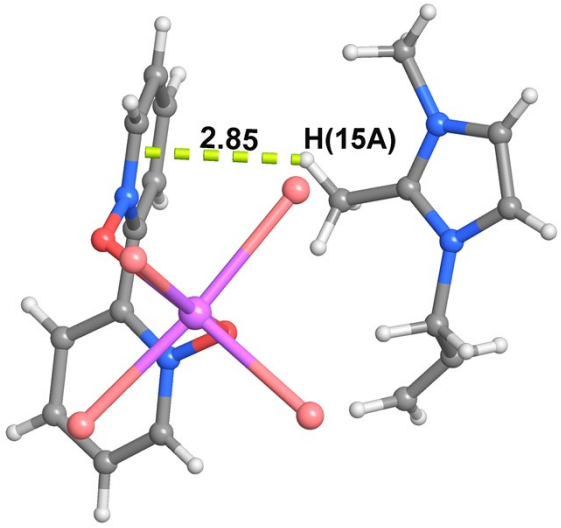

Fig. S8 The view of C−H−π interaction (lime dotted line) for **1**.

Table S8 Selected C−H−π interaction data for **2**.

X−H(I)···Cg(J)	ARU(J)	H···Cg(Å)	<X−H···Cg(°)	X···Cg(Å)	X−H, Pi
C(15)−H(15A)→Cg(1)	4465	2.67	143	3.477(14)	48.00

Cg(1): N(1)→C(1)→C(2)→C(3)→C(4)→C(5). [4465] = -1/2+*x*, 1-*y*, *z*.

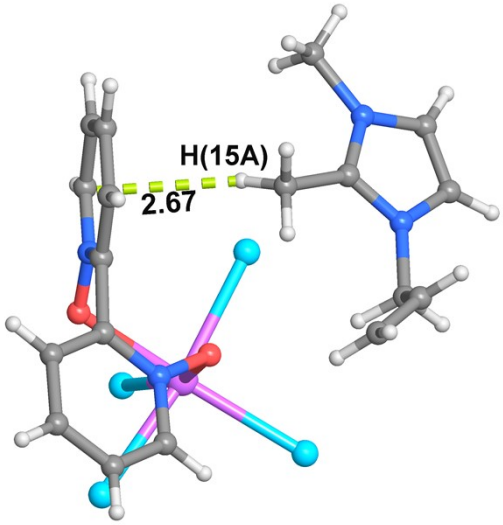

Fig. S9 The view of C−H−π interaction (lime dotted line) for **2**.

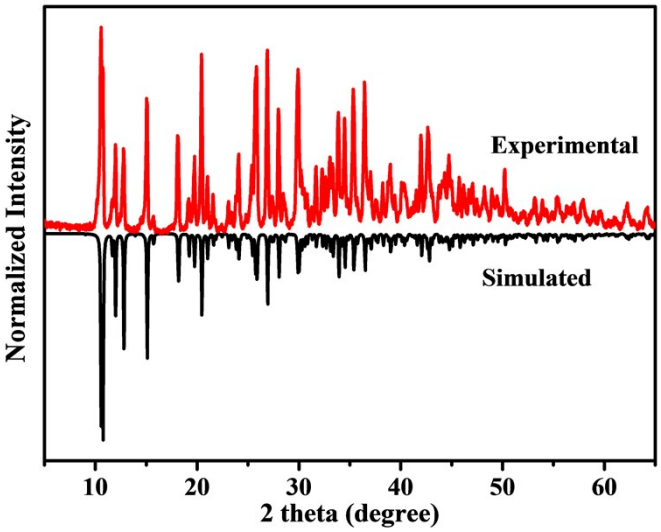

Fig. S10 PXRD patterns of **1**.

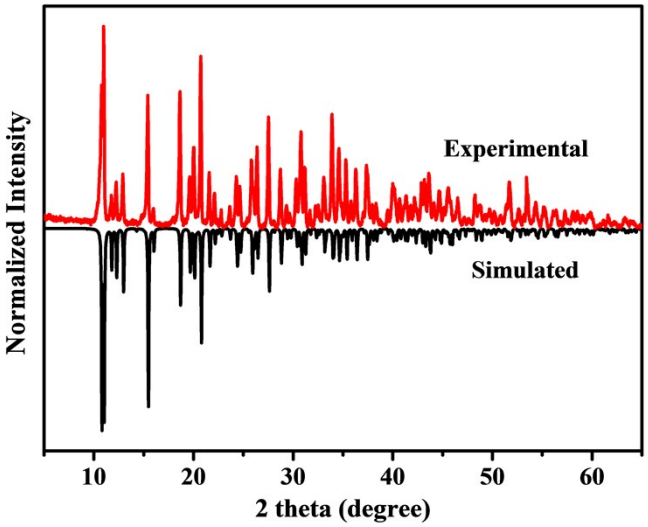

Fig. S11 PXRD patterns of **2**.

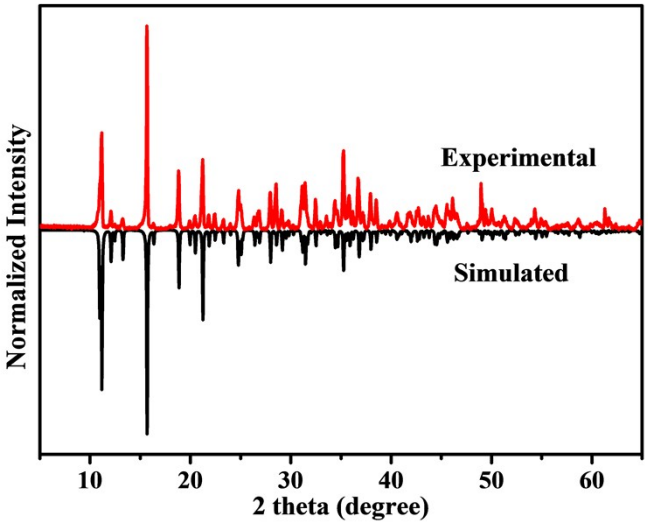

Fig. S12 PXRD patterns of **3**.

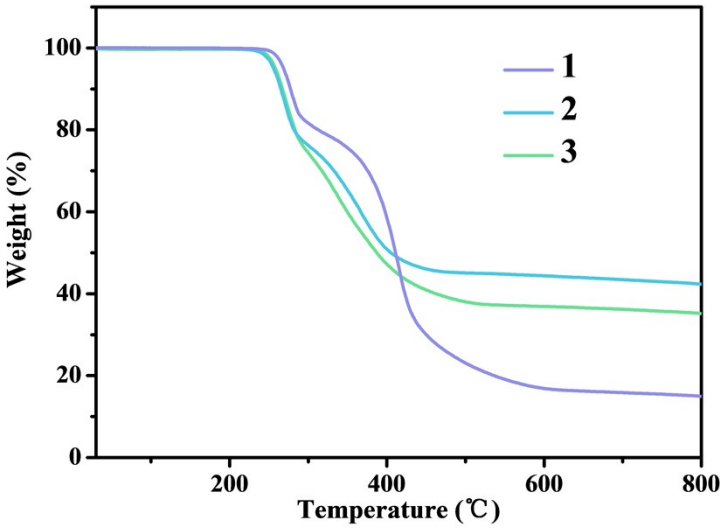

Fig. S13 TG curves of **1**, **2** and **3**.

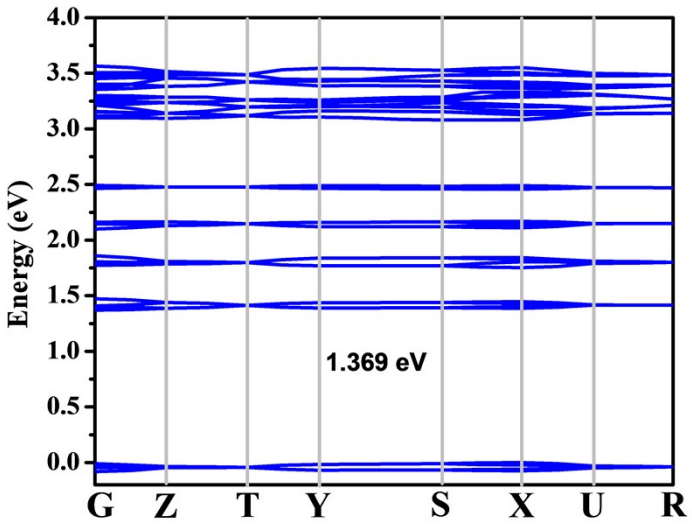

Fig. S14 The electronic band structure of **1**. The calculated bandgap is 1.369 eV.

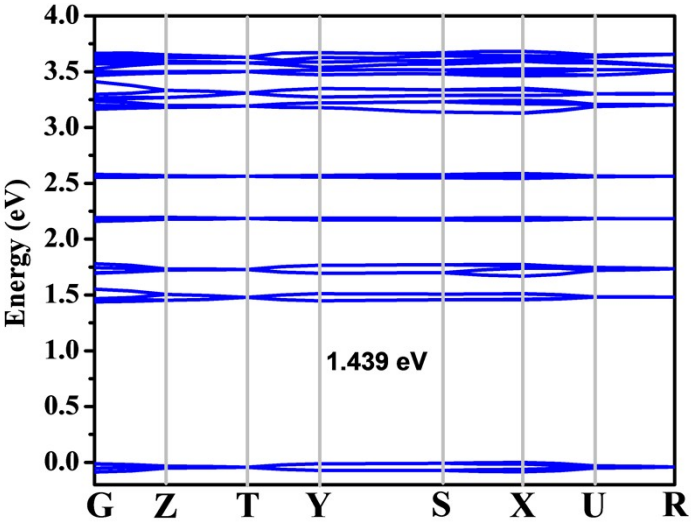

Fig. S15 The electronic band structure of **2**. The calculated bandgap is 1.439 eV.

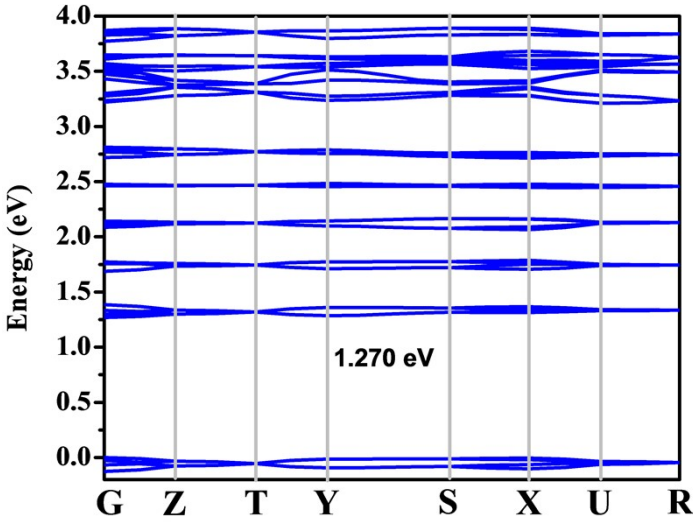

Fig. S16 The electronic band structure of **3**. The calculated bandgap is 1.270 eV.

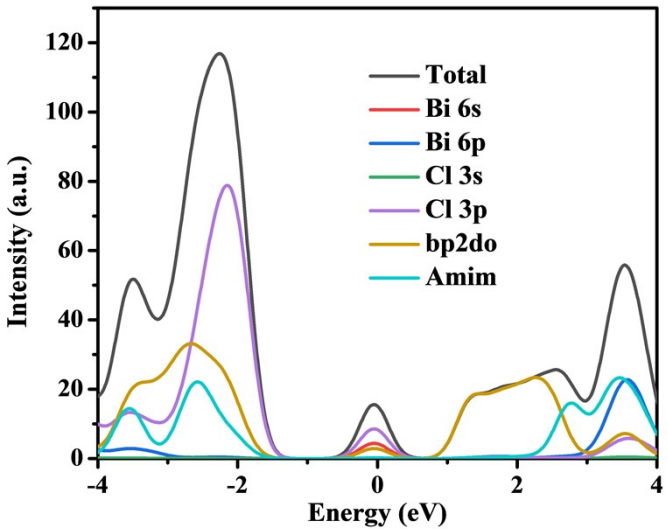

Fig. S17 Density of states (DOSs) for **2**.

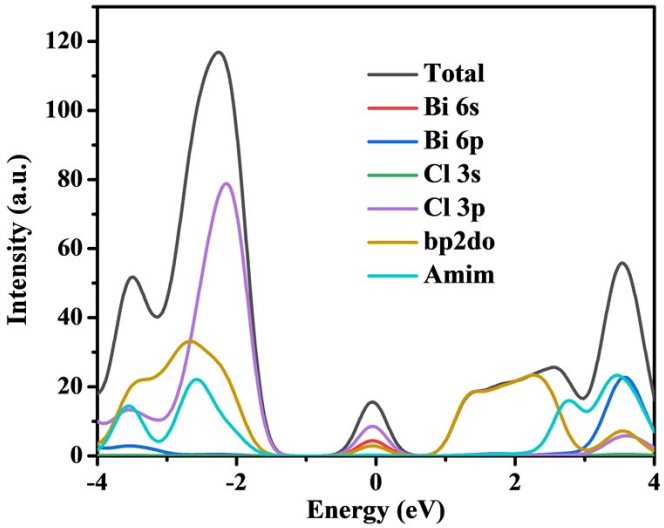

Fig. S18 DOSs for **3**.

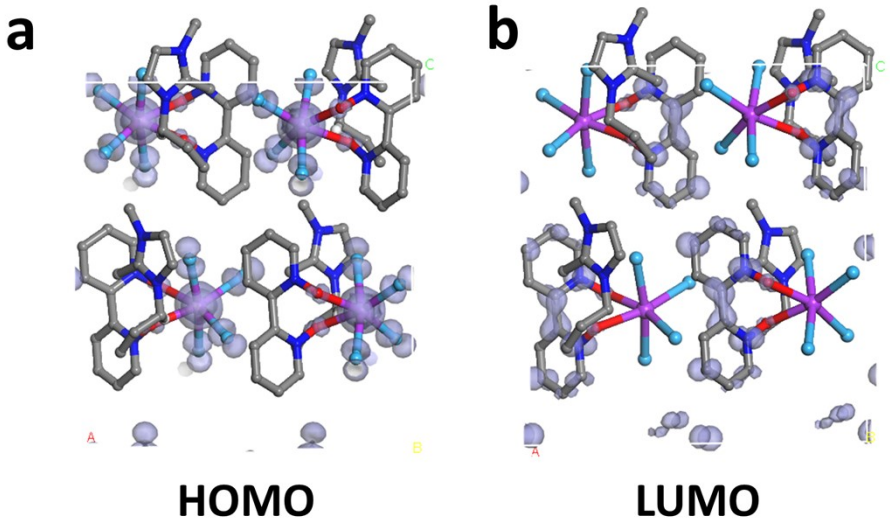

Fig. S19 The molecular orbitals of **2** of the highest occupied molecular orbital (a, HOMO) and the

lowest unoccupied molecular orbital (b, LUMO). The isosurface value is 0.03.

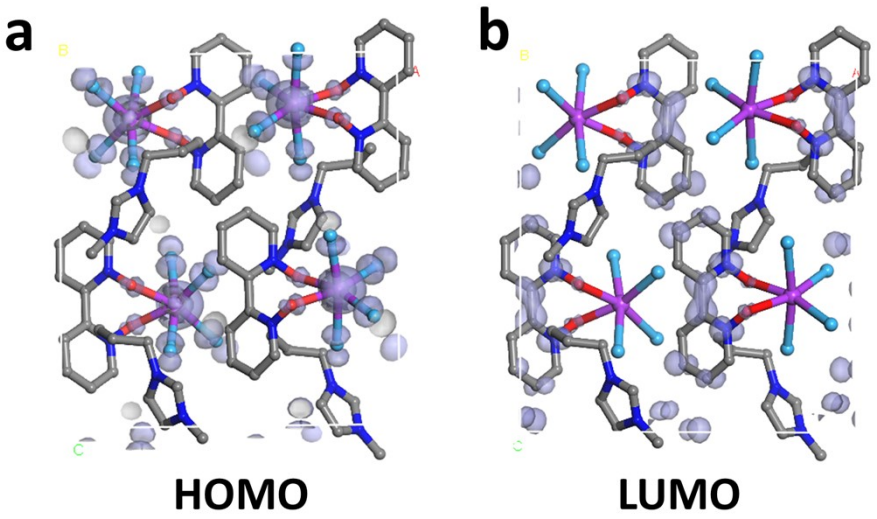

Fig. S20 The molecular orbitals of **3** of HOMO (a) and the LUMO (b). The isosurface value is 0.03.

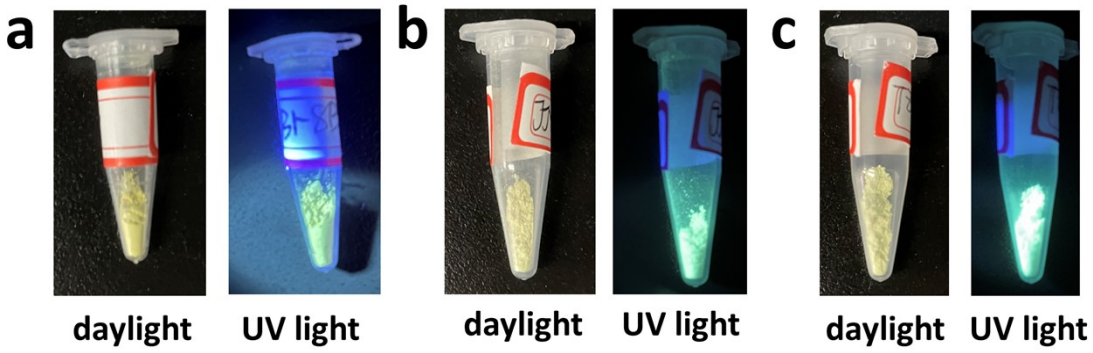

Fig. S21 (a) Photographs of **1** under daylight (left) and UV light (right). (b) Photographs of **2** under daylight (left) and UV light (right). (c) Photographs of **3** under daylight (left) and UV light (right).