Supporting Information

Ionic Indium (III) Chloride Hybrids Incorporating 2,2'-bipyrimidine Ligand: Studies on Photoluminescence and Structural Transformation

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

Compound	**1**	**2**	**3**
Empirical formula	$In_2Cl_8C_{25}H_{33}N_7O$	$In_2Cl_8C_{22}H_{26}N_6$	$In_2Cl_8C_{26}H_{34}N_6$
Formula Mass	960.82	887.73	943.83
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*C*2/*c*	*P*-1	*P*-1
a/Å	17.0310(8)	8.7030(4)	8.5386(6)
b/Å	15.1706(7)	9.1050(5)	10.7576(8)
c/Å	14.2343(7)	10.8430(5)	11.5924(14)
α/°	90	89.960(4)	64.232(9)
β/°	93.138(4)	75.832(4)	73.673(8)
γ/°	90	81.441(4)	83.411(6)
V/Å^3	3672.2(3)	823.22(7)	920.23(16)
Z	4	1	1
T/K	294(2)	290(2)	290(2)
λ/Å	0.71073	0.71073	0.71073
F(000)	1896	434	466
ρ_{calcd}/g cm^{-3}	1.738	1.791	1.703
μ/mm^{-1}	1.869	2.074	1.861
Measured refls.	20828	16207	21945
Independent refls.	4744	3762	5010
No. of parameters	210	173	191
R_{int}	0.0402	0.0539	0.0721
R_1 ($I > 2\sigma(I)$)[a]	0.0301	0.0356	0.0484
$wR(F^2)$ ($I > 2\sigma(I)$)[b]	0.0686	0.0542	0.1093
GOF	1.053	1.008	1.057

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

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

1		**2**		**3**	
In(1)−N(1)	2.370(2)	In(1)−N(1)	2.374(3)	In(1)−N(1)	2.365(3)
In(1)−N(2)#1	2.3696(19)	In(1)−N(2)#1	2.377(3)	In(1)−N(2)#1	2.378(4)
In(1)−Cl(1)	2.4220(7)	In(1)−Cl(1)	2.4541(9)	In(1)−Cl(1)	2.4313(11)
In(1)−Cl(2)	2.4543(8)	In(1)−Cl(2)	2.4329(10)	In(1)−Cl(2)	2.4436(13)
In(1)−Cl(3)	2.4763(8)	In(1)−Cl(3)	2.4336(10)	In(1)−Cl(3)	2.4537(12)
In(1)−Cl(4)	2.4188(7)	In(1)−Cl(4)	2.4751(10)	In(1)−Cl(4)	2.4626(14)
N(1)−In(1)−N(2)#1	69.64(7)	N(1)−In(1)−N(2)#1	69.43(9)	N(1)−In(1)−N(2)#1	69.77(11)
N(1)−In(1)−Cl(1)	162.35(5)	N(1)−In(1)−Cl(1)	85.33(7)	N(1)−In(1)−Cl(1)	162.00(9)
N(1)−In(1)−Cl(2)	83.38(6)	N(1)−In(1)−Cl(2)	164.71(7)	N(1)−In(1)−Cl(2)	84.17(10)

N(1)−In(1)−Cl(3)	84.28(6)	N(1)−In(1)−Cl(3)	89.99(7)	N(1)−In(1)−Cl(3)	93.33(9)
N(1)−In(1)−Cl(4)	93.35(5)	N(1)−In(1)−Cl(4)	83.79(7)	N(1)−In(1)−Cl(4)	84.63(10)
N(2)#1−In(1)−Cl(1)	92.73(5)	N(2)#1−In(1)−Cl(1)	87.47(7)	N(2)#1−In(1)−Cl(1)	92.24(9)
N(2)#1−In(1)−Cl(2)	84.89(6)	N(2)#1−In(1)−Cl(2)	95.34(7)	N(2)#1−In(1)−Cl(2)	86.96(10)
N(2)#1−In(1)−Cl(3)	82.31(6)	N(2)#1−In(1)−Cl(3)	158.83(7)	N(2)#1−In(1)−Cl(3)	162.72(9)
N(2)#1−In(1)−Cl(4)	162.87(5)	N(2)#1−In(1)−Cl(4)	79.17(7)	N(2)#1−In(1)−Cl(4)	82.93(10)
Cl(1)−In(1)−Cl(2)	94.84(3)	Cl(1)−In(1)−Cl(4)	165.08(4)	Cl(1)−In(1)−Cl(2)	95.00(4)
Cl(1)−In(1)−Cl(3)	94.16(3)	Cl(2)−In(1)−Cl(1)	92.91(4)	Cl(1)−In(1)−Cl(3)	104.64(4)
Cl(2)−In(1)−Cl(3)	164.67(3)	Cl(2)−In(1)−Cl(3)	105.30(4)	Cl(1)−In(1)−Cl(4)	93.60(5)
Cl(4)−In(1)−Cl(1)	104.30(3)	Cl(2)−In(1)−Cl(4)	94.90(4)	Cl(2)−In(1)−Cl(3)	95.08(5)
Cl(4)−In(1)−Cl(2)	95.38(3)	Cl(3)−In(1)−Cl(1)	95.99(4)	Cl(2)−In(1)−Cl(4)	166.97(5)
Cl(4)−In(1)−Cl(3)	94.39(3)	Cl(3)−In(1)−Cl(4)	94.19(4)	Cl(3)−In(1)−Cl(4)	92.19(5)
C(1)−N(1)−In(1)	125.17(16)	C(1)−N(1)−In(1)	125.4(2)	C(1)−N(1)−In(1)	125.7(3)
C(4)−N(1)−In(1)	117.79(16)	C(4)−N(1)−In(1)	117.3(2)	C(4)−N(1)−In(1)	117.9(3)
C(3)−N(2)−In(1)#1	124.78(16)	C(3)−N(2)−In(1)#1	125.3(2)	C(3)−N(2)−In(1)#1	125.2(3)
C(4)−N(2)−In(1)#1	117.84(15)	C(4)−N(2)−In(1)#1	116.7(2)	C(4)−N(2)−In(1)#1	117.4(3)
Symmetry transformations used to generate equivalent atoms:					
#1 -*x*+1/2, -*y*+1/2, -*z*+1		#1 -*x*+1, -*y*, -*z*+1		#1 -*x*, -*y*+2, -*z*+1	

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

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<(DHA) (°)
1				
H-bonds in anions				
C(1)−H(1)···Cl(1)#2	0.93	2.86	3.499(3)	126.5
C(1)−H(1)···Cl(4)	0.93	2.92	3.539(3)	124.9
C(3)−H(3)···Cl(1)#1	0.93	2.88	3.506(3)	125.5
C(3)−H(3)···Cl(4)#3	0.93	2.90	3.512(3)	124.8
H-bonds between anions and cations				
C(5)−H(5)···Cl(2)#4	0.93	2.69	3.609(4)	172.2
C(6)−H(6)···Cl(3)#5	0.93	2.83	3.589(4)	139.8
C(8)−H(8)···Cl(2)#6	0.93	2.94	3.612(4)	130.1
C(9)−H(9)···Cl(3)#7	0.93	2.65	3.539(4)	159.2
C(10)−H(10A)···Cl(4)#4	0.97	2.92	3.814(7)	154.1
C(10)−H(10B)···Cl(1)#7	0.97	2.85	3.698(6)	146.1
C(11)−H(11C)···Cl(3)	0.96	2.89	3.814(5)	161.4
H-bonds between anions and solvent molecule				
C(13^a)−H(13B^a)···Cl(1)#7	0.96	3.07	3.61(3)	117.2
Symmetry transformations used to generate equivalent atoms:				
#1 -*x*+1/2, -*y*+1/2, -*z*+1; #2 -*x*+1/2, *y*-1/2, -*z*+1/2; #3 *x*, -*y*, *z*+1/2; #4 *x*+1/2, -*y*+1/2 , *z*+1/2; #5 -*x*+1, -*y*, -*z*+1; #6 *x*+1/2, *y*-1/2, *z*; #7 -*x*+1, *y*, -*z*+1/2.				
2				
H-bonds in anions				
C(1)−H(1)···Cl(1)#2	0.93	2.83	3.589(3)	139.8
C(1)−H(1)···Cl(3)	0.93	2.85	3.432(4)	121.4

C(3)−H(3)···Cl(1)#3	0.93	2.93	3.559(4)	126.3
H-bonds between anions and cations				
C(5)−H(5)···Cl(3)#2	0.93	2.83	3.749(5)	169.2
C(6)−H(6)···Cl(2)#4	0.93	2.92	3.773(5)	152.8
C(9)−H(9)···Cl(2)#5	0.93	2.96	3.461(4)	115.3
C(9)−H(9)···Cl(4)#6	0.93	2.87	3.522(5)	127.8
C(11)−H(11B)···Cl(4)#6	0.96	2.96	3.699(5)	135.1
C(11)−H(11C)···Cl(4)#1	0.96	2.91	3.627(4)	132.6
Symmetry transformations used to generate equivalent atoms:				
#1 -*x*+1, -*y*, -*z*+1; #2 -*x*+1, -*y*+1, -*z*+1; #3 *x*-1, *y*, *z*; #4 -*x*+2, -*y*+1, -*z*+1; #5 -*x*+2, -*y*, -*z*+1; #6 *x*, *y*, *z*+1.				
3				
H-bonds in anions				
C(1)−H(1)···Cl(3)	0.93	2.94	3.562(5)	125.1
C(3)−H(3)···Cl(1)#1	0.93	2.88	3.506(5)	125.4
C(3)−H(3)···Cl(2)#2	0.93	2.91	3.554(4)	127.3
H-bonds between anions and cations				
C(6)−H(6)···Cl(3)#3	0.93	2.87	3.615(7)	137.5
C(8)−H(8)···Cl(4)#4	0.93	2.82	3.719(6)	162.2
C(9)−H(9)···Cl(1)#4	0.93	2.81	3.507(6)	132.4
C(10)−H(10A)···Cl(4)#5	0.97	2.74	3.602(7)	148.4
C(10)−H(10B)···Cl(3)	0.97	2.94	3.766(7)	144.2
Symmetry transformations used to generate equivalent atoms:				
#1 -*x*, -*y*+2, -*z*+1; #2 *x*-1, *y*, *z*; #3 -*x*+1, -*y*+1, -*z*+1; #4 -*x*+1, -*y*+1, -*z*+2; #5 -*x*, -*y*+1, -*z*+2.				

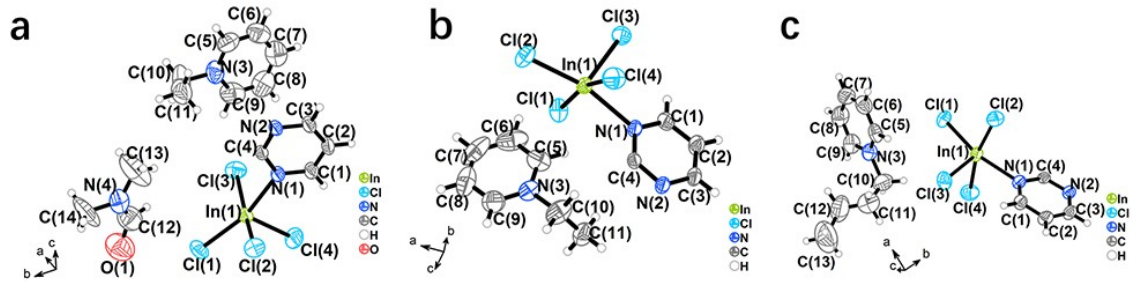

Figure S1 *ORTEP* drawings (50% ellipsoid probability) of the asymmetric units of **1** (a), **2** (b) and **3** (c).

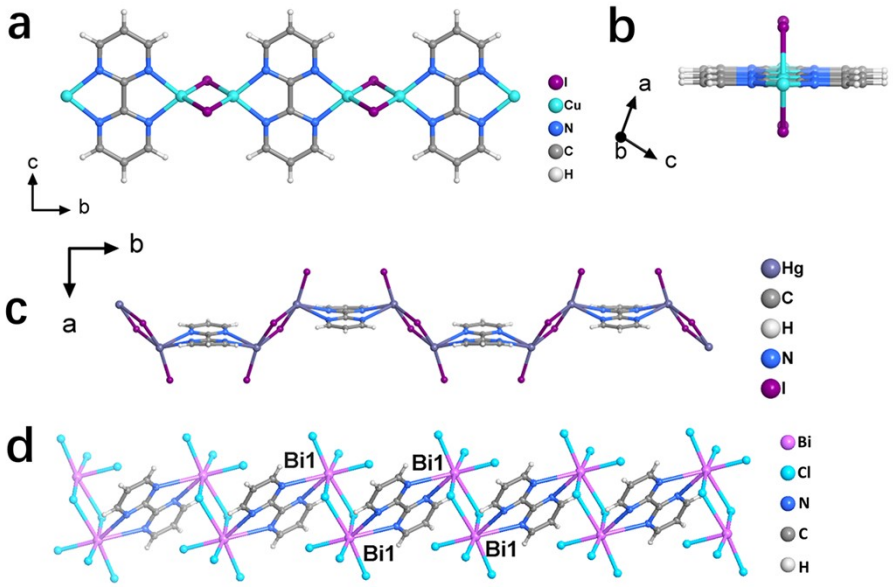

Figure S2 Views of the structure of $[(CuI)_2(bpym)]$[1] along the *a* axis (a) and *b* axis (b). (c) View of the structure of $[Hg_2I_4(bpym)]$[2] along the *c* axis. (d) View of the anionic chain in $[ILC][Bi_2Cl_8(bpym)]$[3] (*ILC* = BPy, *N*-butylpyridinium or EPy, *N*-ethylpyridinium).

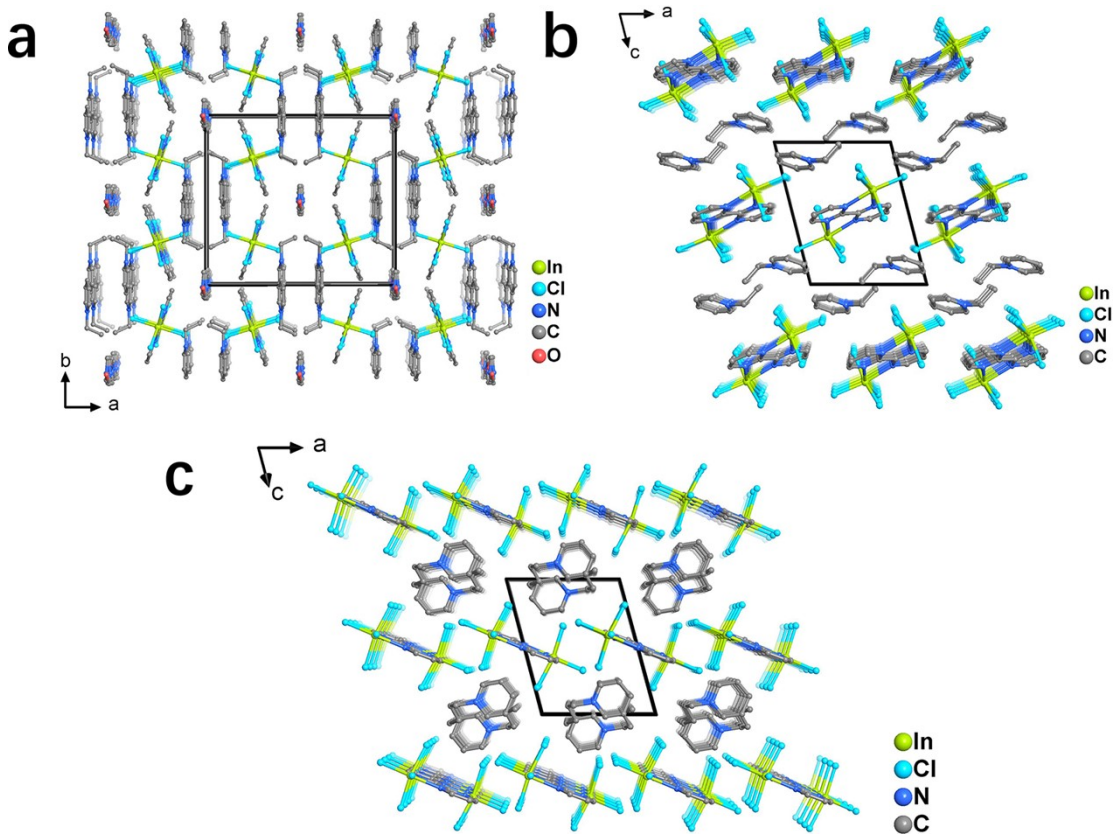

Figure S3 View of structural packing modes for **1** (a) along the *c* axis, **2** (b) along the *b* axis and **3** (c) along the *b* axis. H atoms are omitted for clarity.

Table S4 The π–π interaction data for **1** at 294 K.

Cg(I)···Cg(J)	ARU(J)	Cg···Cg(Å)	α(°)	β(°)	γ(°)
Cg(3)→Cg(4)	3656	4.184(2)	21.60	20.13	40.93
Cg(4)→Cg(3)	3656	4.184(2)	21.60	40.93	20.13
Cg(4)→Cg(4)	3656	3.810(2)	0.02	24.69	24.69
Cg(3): N(1)→C(1)→C(2)→C(3)→N(2)→C(4); Cg(4): N(3)→C(5)→C(6)→C(7)→C(8)→C(9).					

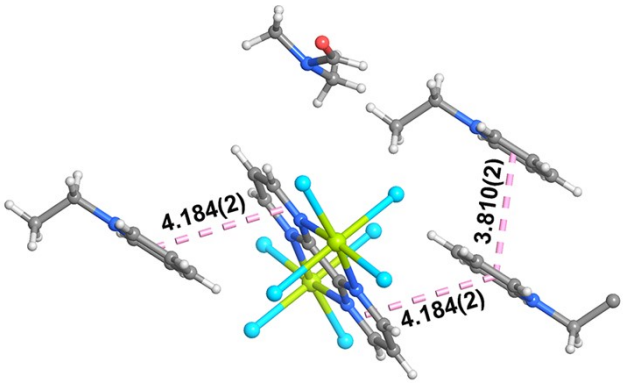

Figure S4 π–π interactions shown in rose dotted lines for **1**. The ring-to-ring distances are 3.810(2) and 4.184(2) Å.

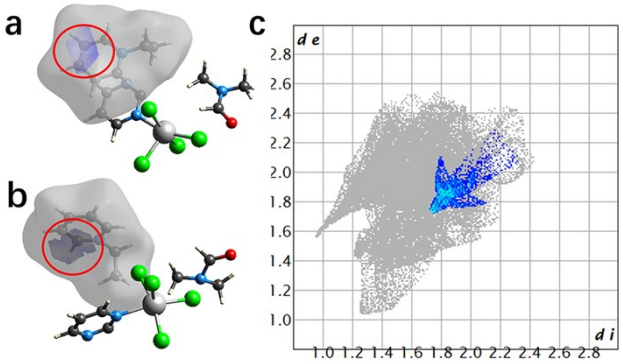

Figure S5 The Hirshfeld d_{norm} surfaces of organic part with C···C interaction for **1** (a) and viewed from behind (b). The C···C interaction for **1** is circled in red. (c) 2D fingerprint plot of C···C interaction for **1**. The fingerprint covers from *di* = *de* = 1.8 to 2.0 Å.

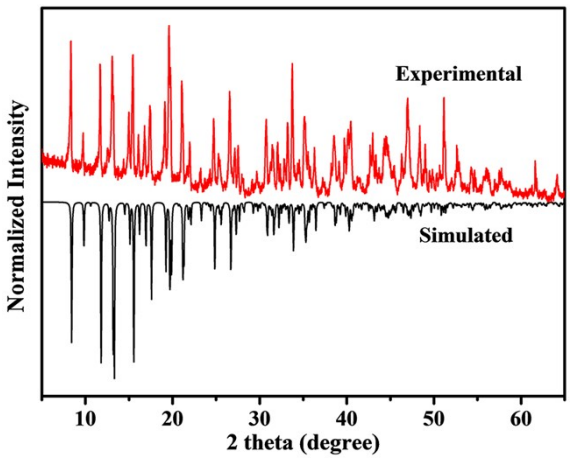

Figure S6 Experimental and simulated PXRD patterns of **2**.

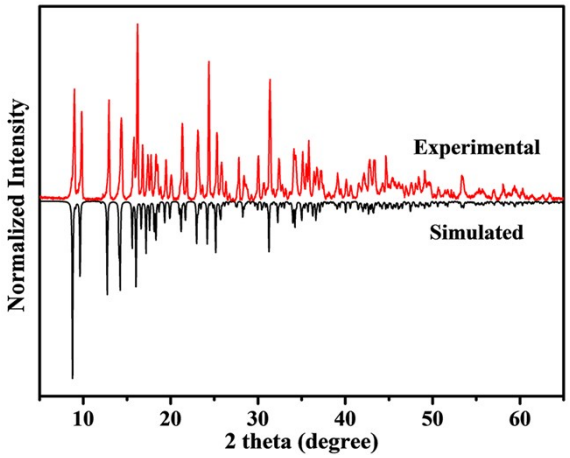

Figure S7 Experimental and simulated PXRD patterns of **3**.

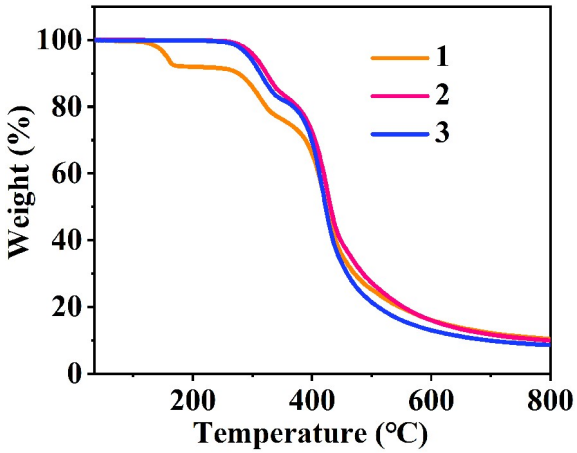

Figure S8 TG curves for **1**, **2** and **3**.

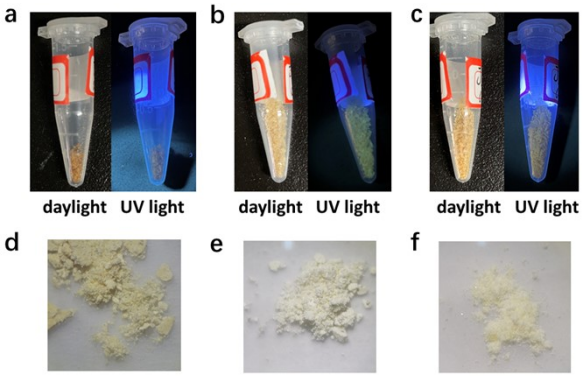

Figure S9 Photographs of crystals under daylight (left) and UV irradiation (right) for **1** (a), **2** (b) and **3** (c). Photographs of powdered samples obtained by grinding crystals **1** (d), **2** (e) and **3** (f).

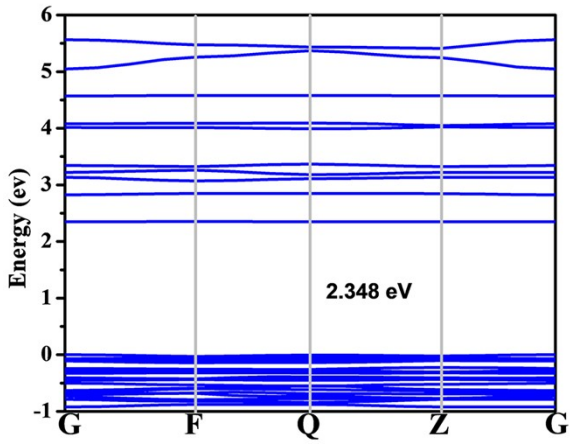

Figure S10 The electronic band structure of **2**. The calculated bandgap of **2** is 2.348 eV.

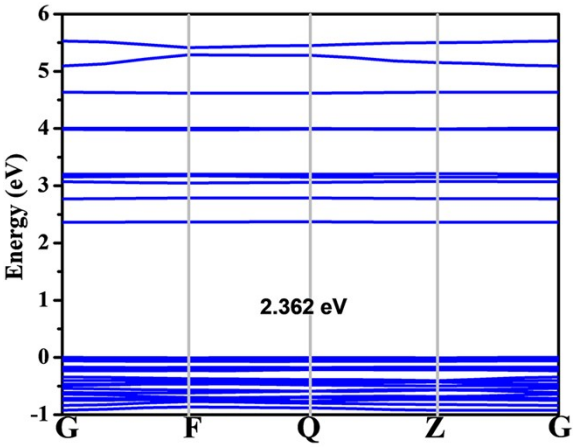

Figure S11 The electronic band structure of **3**. The calculated bandgap of **3** is 2.362 eV.

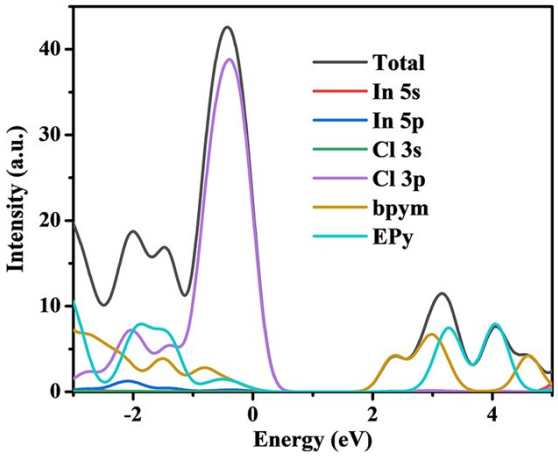

Figure S12 Density of states (DOSs) of **2**.

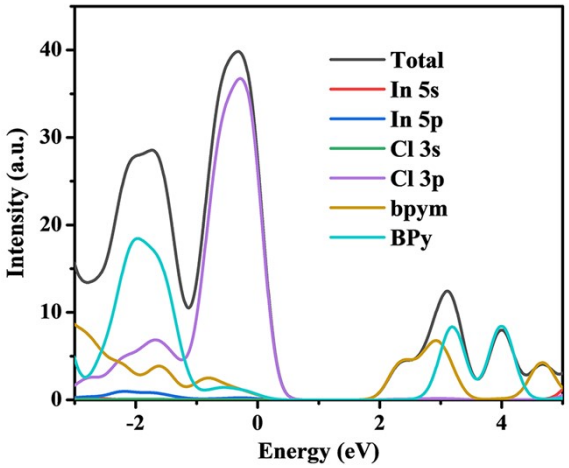

Figure S13 DOSs of **3**.

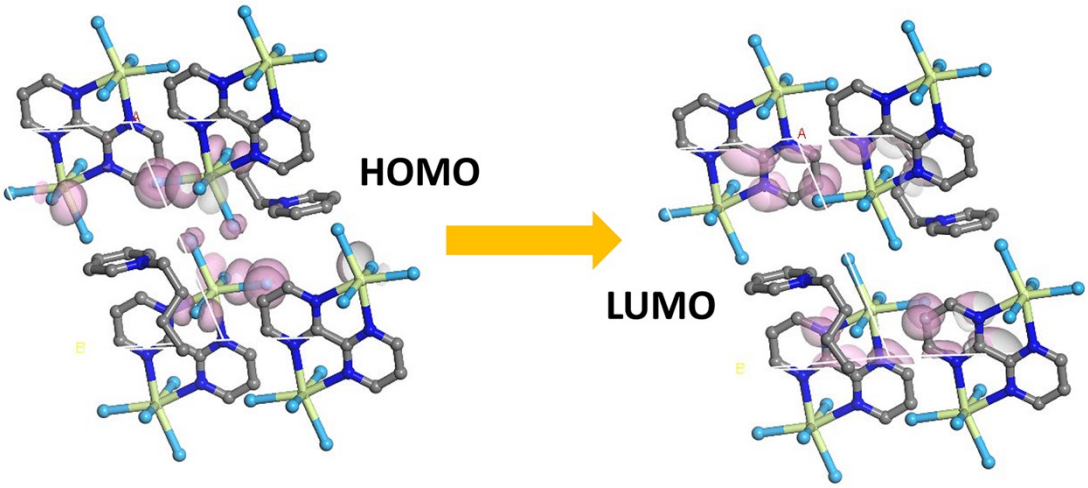

Figure S14 The highest occupied molecular orbital (HOMO, left) and the lowest unoccupied molecular orbital (LUMO, right) for **3**. The isosurface values are 0.03.

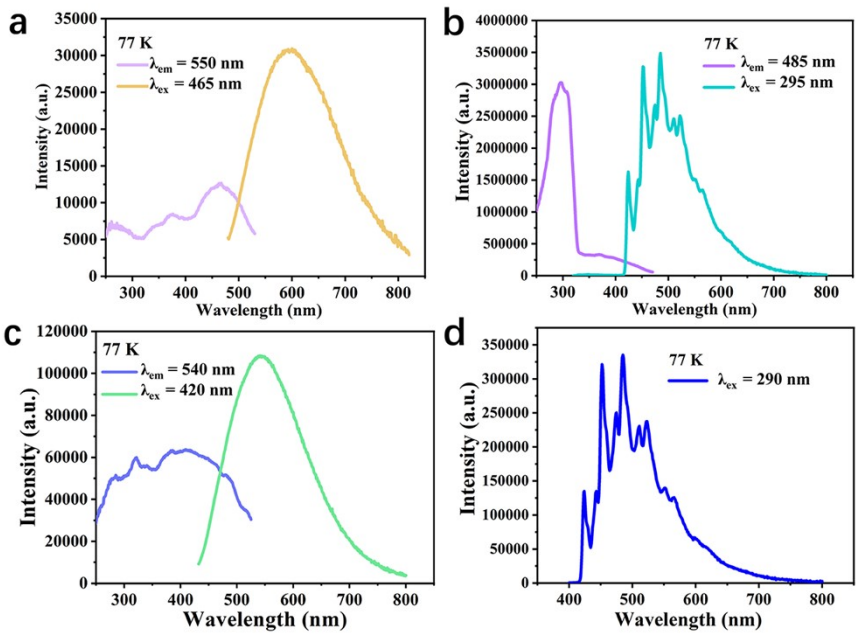

Figure S15 The PLE and PL spectra at 77 K for **1** (a), **2** (b) and **3** (c). The PL spectrum of **1-h** at 77 K. Note that the PL spectra for **2** and **1-h** at 77 K are comparable except the difference in PL intensity.

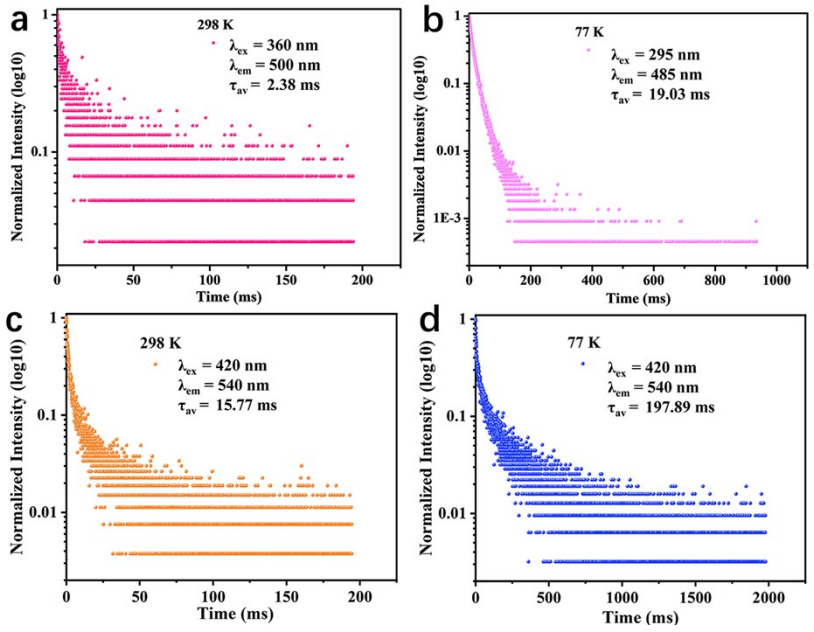

Figure S16 The PL decay spectra of **2** at 298 K (a) and at 77 K (b) and of **3** at 298 K(c) and at 77 K (d).

References

1. F. Hou, M. Powel, D. B. Dougherty, R. D. Sommer and P. A. Maggard, *Cryst. Growth Des.*, 2018, **18**, 5406-5416.
2. E. Priola, E. Bonometti, V. Brunella, L. Operti and E. Diana, *Polyhedron*, 2016, **104**, 25-36.
3. J.-C. Jin, N.-N. Shen, Y.-P. Lin, L.-K. Gong, H.-Y. Tong, K.-Z. Du and X.-Y. Huang, *Inorg. Chem.*, 2020, **59**, 13465-13472.