Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Modulating the structure and photochromic performance of hybrid metal chloride with nonphotochromic 1,10-phenanthroline and its derivative

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Instrumentation

Elemental analyses (EA, C, H, and N) were measured on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). Thermogravimetric analysis (TGA) was measured on a Rigaku Thermo plus EVO2 TG-DTA 8121 analyzer under an air atmosphere. 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 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. The Xe-lamp for photochromic characterization is a Perfect Light PLS-SXE 300. To assure the adequate photoactivation for ET, the irradiation time was enlarged to 100 min before magnetic characterizations. The magnetic data were gauged on a Quantum Design SQUID (MPMS-XL-7) magnetometer. The resulting data have been corrected with Pascal's constants.

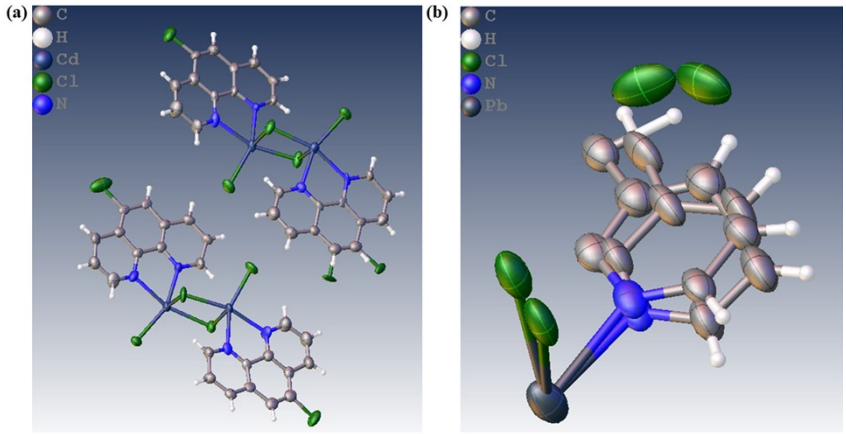

Fig. S1 The disordered 5-Cl-phen ligand for complexes **5** (a) and **6** (b).

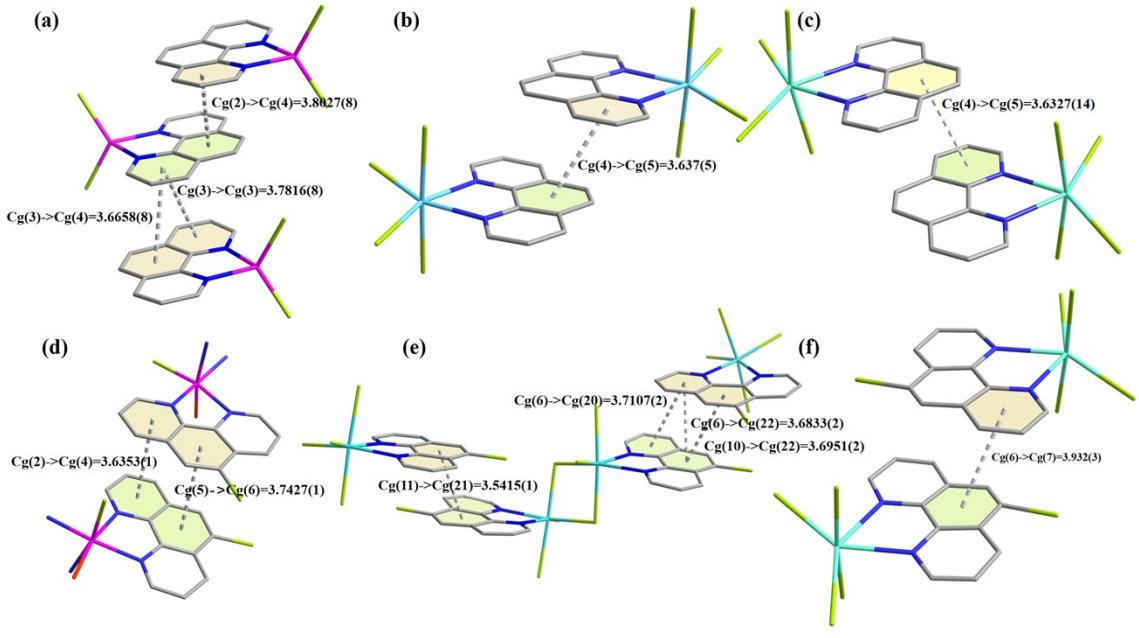

Fig. S2 The π···π stacking interactions for complexes **1**-**6**.

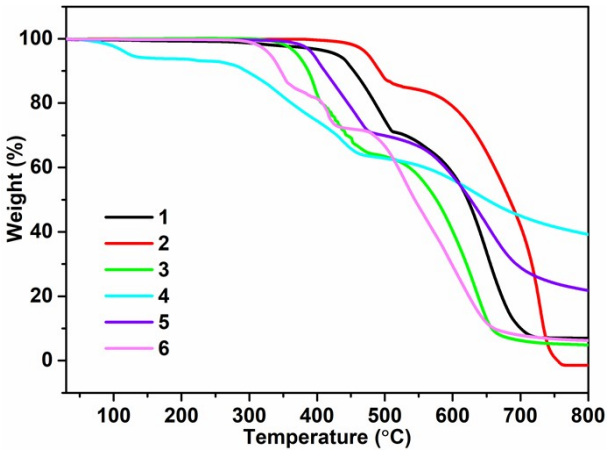

Fig. S3 TGA pattern of **1-6**.

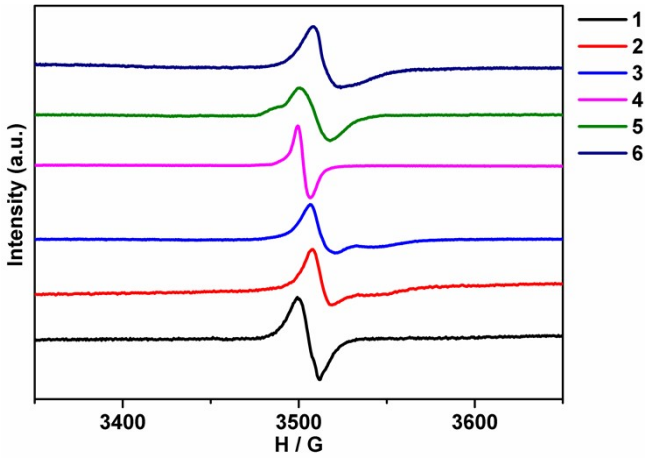

Fig. S4 The EPR plots of **1-6**.

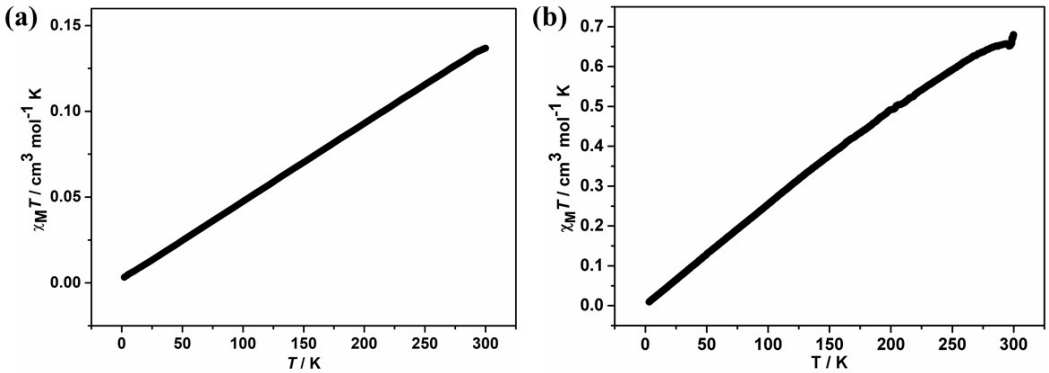

Fig. S5 The $\chi_M T$ *vs.* *T* plots of the photoactivated samples of **1** (a) and **4** (b).

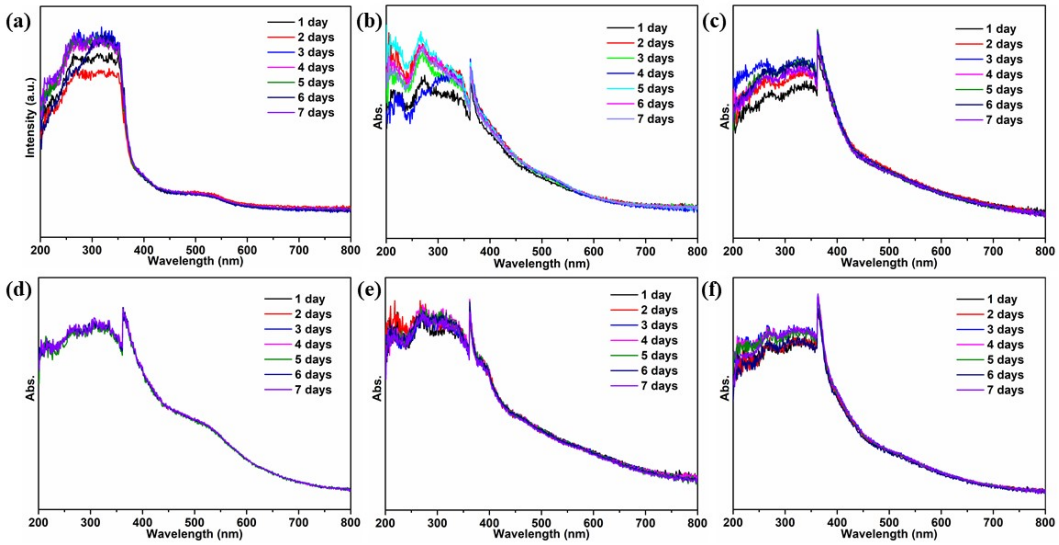

Fig. S6 The time-dependent UV-Vis spectra of **1** (a), **2** (b), **3** (c), **4** (d), **5** (e) and **6** (f).

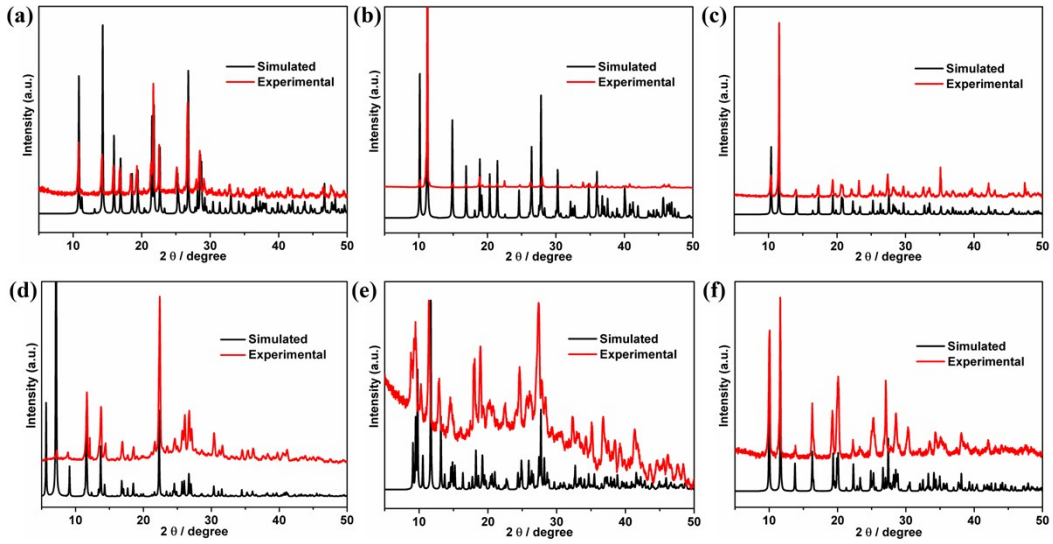

Fig. S7 PXRD patterns of **1** (a), **2** (b), **3** (c), **4** (d), **5** (e) and **6** (f).

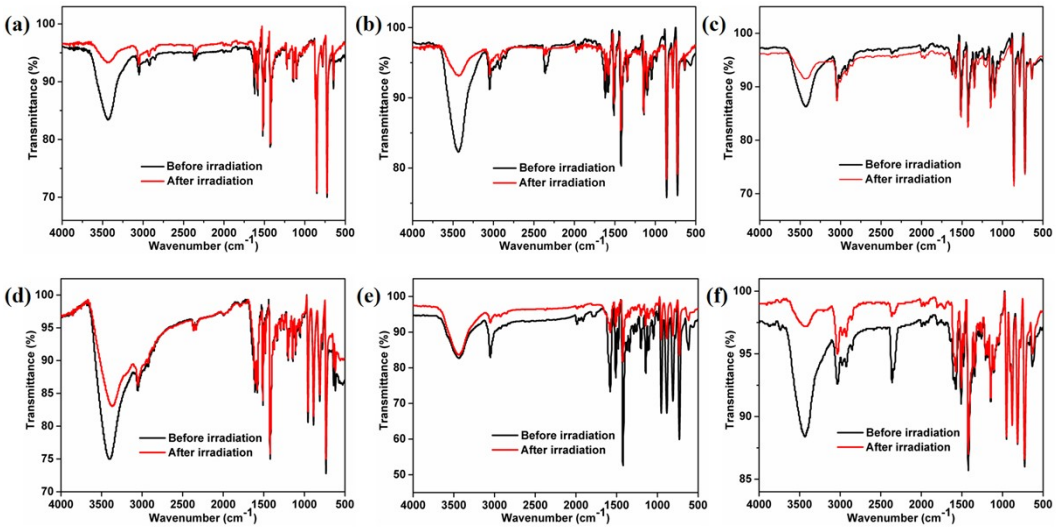

Fig. S8 IR patterns of **1** (a), **2** (b), **3** (c), **4** (d), **5** (e) and **6** (f).

Table S1. SHAPE analysis of the metal ions in **1-6.**

Metal	Label	Shape	Symmetry	Distortion
1-Zn1	SP-4	Square	D_{4h}	24.621
1-Zn1	T-4	Tetrahedron	T_d	3.042
1-Zn1	SS-4	Seesaw	C_{2v}	7.12
2-Cd1	HP-6	Hexagon	D_{6h}	32.519
2-Cd1	PPY-6	Pentagonal pyramid	C_{5v}	24.086
2-Cd1	OC-6	Octahedron	O_h	1.934
2-Cd1	TPR-6	Trigonal prism	D_{3h}	12.544
2-Cd1	JPPY-6	Johnson pentagonal pyramid J2	C_{5v}	28.399
3-Pb1	HP-6	Hexagon	D_{6h}	33.225
3-Pb1	PPY-6	Pentagonal pyramid	C_{5v}	24.836
3-Pb1	OC-6	Octahedron	O_h	4.495
3-Pb1	TPR-6	Trigonal prism	D_{3h}	12.252
3-Pb1	JPPY-6	Johnson pentagonal pyramid J2	C_{5v}	26.486
4-Zn1	HP-6	Hexagon	D_{6h}	33.392
4-Zn1	PPY-6	Pentagonal pyramid	C_{5v}	22.443
4-Zn1	OC-6	Octahedron	O_h	2.490
4-Zn1	TPR-6	Trigonal prism	D_{3h}	11.594
4-Zn1	JPPY-6	Johnson pentagonal pyramid J2	C_{5v}	26.479
5-Cd1	HP-6	Hexagon	D_{6h}	33.301
5-Cd1	PPY-6	Pentagonal pyramid	C_{5v}	19.448
5-Cd1	OC-6	Octahedron	O_h	2.765
5-Cd1	TPR-6	Trigonal prism	D_{3h}	10.601
5-Cd1	JPPY-6	Johnson pentagonal pyramid J2	C_{5v}	23.716
5-Cd2	HP-6	Hexagon	D_{6h}	50.022
5-Cd2	PPY-6	Pentagonal pyramid	C_{5v}	36.842

5-Cd2	OC-6	Octahedron	O_h	32.270
5-Cd2	TPR-6	Trigonal prism	D_{3h}	39.447
5-Cd2	JPPY-6	Johnson pentagonal pyramid J2	C_{5v}	40.134
5-Cd3	HP-6	Hexagon	D_{6h}	33.337
5-Cd3	PPY-6	Pentagonal pyramid	C_{5v}	23.843
5-Cd3	OC-6	Octahedron	O_h	2.165
5-Cd3	TPR-6	Trigonal prism	D_{3h}	11.521
5-Cd3	JPPY-6	Johnson pentagonal pyramid J2	C_{5v}	27.336
5-Cd4	HP-6	Hexagon	D_{6h}	53.119
5-Cd4	PPY-6	Pentagonal pyramid	C_{5v}	35.658
5-Cd4	OC-6	Octahedron	O_h	35.288
5-Cd4	TPR-6	Trigonal prism	D_{3h}	38.243
5-Cd4	JPPY-6	Johnson pentagonal pyramid J2	C_{5v}	40.704
6-Pb1	HP-6	Hexagon	D_{6h}	31.046
6-Pb1	PPY-6	Pentagonal pyramid	C_{5v}	24.746
6-Pb1	OC-6	Octahedron	O_h	3.020
6-Pb1	TPR-6	Trigonal prism	D_{3h}	14.619
6-Pb1	JPPY-6	Johnson pentagonal pyramid J2	C_{5v}	26.704

Table S2 Details of selected hydrogen bond in **1**

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (deg)
C(3)-H(3)···Cl(2)	0.93	2.81	3.6743(8)	156
C(6)-H(6)···Cl(2)	0.93	2.80	3.5175(7)	135

Table S3 Details of selected hydrogen bond in **2**

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (deg)
C(2)-H(2)···Cl(1)	0.93	2.75	3.651(13)	164
C(6)-H(6)···Cl(1)	0.93	2.78	3.671(9)	162

Table S4 Details of selected hydrogen bond in **3**

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (deg)
C(2)-H(2)···Cl(1)	0.931	2.773	3.686	166.88
C(5)-H(4)···Cl(1)	0.929	2.834	3.744	166.63

Table S5 Details of selected hydrogen bond in **4**

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (deg)
C(8)-H(8)···Cl(4)	0.93	2.57	3.4010(1)	149
C(14)-H(14)···Cl(4)	0.93	2.81	3.4753(1)	129

Table S6 Details of selected hydrogen bond in **5**

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (deg)
C00K-H00K···Cl07	0.93	2.67	3.3559(1)	132
C00O-H00O···Cl0C	0.93	2.80	3.5104(1)	134
C013-H013···Cl09	0.93	2.83	3.4007(1)	121
C016-H016···Cl0A	0.93	2.62	3.4770(1)	153
C01Y-H01Y···Cl06	0.93	2.72	3.5084(1)	143
C021-H021···Cl08	0.93	2.62	3.5235(1)	164
C022-H022···Cl09	0.93	2.73	3.3490(1)	125

Table S7 Details of selected hydrogen bond in **6**

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (deg)
C(2)-H(2)···Cl(2A)	0.93	2.79	3.44(3)	128
C(2)-H(2)···Cl(2B)	0.93	2.77	3.61(3)	150
C(2A)-H(2A)···Cl(2A)	0.93	2.59	3.48(3)	161

Table S8 Selected bond lengths (Å) and angles (°) for **1**

Zn(1)-Cl(1)	2.2053(11)	Zn(1)-N(1)	2.055(3)
Zn(1)-Cl(2)	2.2083(11)	Zn(1)-N(2)	2.072(3)
Cl(1)-Zn(1)-Cl(2)	114.77(4)	N(1)-Zn(1)-N(2)	81.09(11)
N(1)-Zn(1)-Cl(1)	108.69(8)	N(2)-Zn(1)-Cl(1)	124.68(9)
N(1)-Zn(1)-Cl(2)	115.87(9)	N(2)-Zn(1)-Cl(2)	107.61(5)

Table S9 Selected bond lengths (Å) and angles (°) for **2**

Cd(1)-Cl(1)	2.552(2)	Cd(1)-Cl(1)#3	2.753(2)
Cd(1)-Cl(1)#1	2.552(2)	Cd(1)-N(1)	2.353(6)
Cd(1)-Cl(1)#2	2.753(2)	Cd(1)-N(1)#1	2.353(6)

Cl(1)#2-Cd(1)-Cl(1)#1	84.90(10)	N(1)#1-Cd(1)-Cl(1)#2	85.8(2)
Cl(1)#2-Cd(1)-Cl(1)#3	177.40(10)	N(1)#1-Cd(1)-Cl(1)#3	92.1(2)
Cl(1)#3-Cd(1)-Cl(1)#1	96.70(10)	N(1)-Cd(1)-Cl(1)	161.1(2)
Cl(1)-Cd(1)-Cl(1)#1	104.40(10)	N(1)-Cd(1)-Cl(1)#1	93.0(2)
Cl(1)-Cd(1)-Cl(1)#2	96.70(10)	N(1)-Cd(1)-Cl(1)#2	92.1(2)
Cl(1)-Cd(1)-Cl(1)#3	84.90(10)	N(1)-Cd(1)-Cl(1)#3	85.8(2)
N(1)#1-Cd(1)-Cl(1)	93.0(2)	N(1)-Cd(1)-N(1)#1	70.9(3)
N(1)#1-Cd(1)-Cl(1)#1	161.1(2)		

Table S10 Selected bond lengths (Å) and angles (°) for 3

Pb(1)-Cl(1)	2.844(4)	Pb(1)-Cl(1)#3	3.017(3)
Pb(1)-Cl(1)#1	2.844(4)	Pb(1)-N(1)	2.505(10)
Pb(1)-Cl(1)#2	3.017(3)	Pb(1)-N(1)#1	2.505(10)
Cl(1)#1-Pb(1)-Cl(1)	167.19(16)	N(1)#1-Pb(1)-Cl(1)#2	84.8(2)
Cl(1)#1-Pb(1)-Cl(1)#2	87.41(10)	N(1)#1-Pb(1)-Cl(1)#3	150.2(2)
Cl(1)#1-Pb(1)-Cl(1)#3	98.58(11)	N(1)#1-Pb(1)-N(1)	66.7(5)
Cl(1)#2-Pb(1)-Cl(1)#3	124.49(15)	N(1)-Pb(1)-Cl(1)	86.8(2)
Cl(1)-Pb(1)-Cl(1)#2	98.57(11)	N(1)-Pb(1)-Cl(1)#1	82.5(2)
Cl(1)-Pb(1)-Cl(1)#3	87.41(10)	N(1)-Pb(1)-Cl(1)#2	150.2(2)
N(1)#1-Pb(1)-Cl(1)	82.5(2)	N(1)-Pb(1)-Cl(1)#3	84.8(2)
N(1)#1-Pb(1)-Cl(1)#1	86.8(2)		

Symmetry codes: #1: -x+2, y, -z+1/2; #2: x, -y+1, z+1/2; #3: -x+2, -y+1, -z.

Table S11 Selected bond lengths (Å) and angles (°) for 4

Zn(1)-Cl(3)	2.357(2)	Zn(1)-N(2A)	1.998(15)
Zn(1)-N(1)	2.222(4)	Zn(1)-N(4)	2.148(6)
Zn(1)-N(1A)	2.046(16)	Zn(1)-N(5)	2.215(5)
Zn(1)-N(2)	2.168(4)	Zn(1)-O(1)	2.092(6)
N(1)-Zn(1)-Cl(3)	165.92(15)	N(2A)-Zn(1)-O(1)	76.6(6)
N(1A)-Zn(1)-Cl(3)	111.1(4)	N(4)-Zn(1)-Cl(3)	92.83(19)
N(1A)-Zn(1)-N(4)	154.7(5)	N(4)-Zn(1)-N(1)	101.1(2)
N(1A)-Zn(1)-N(5)	93.2(7)	N(4)-Zn(1)-N(2)	165.8(2)
N(1A)-Zn(1)-O(1)	95.7(7)	N(4)-Zn(1)-N(5)	76.2(2)
N(2)-Zn(1)-Cl(3)	91.87(16)	N(5)-Zn(1)-Cl(3)	94.61(14)
N(2)-Zn(1)-N(1)	75.0(2)	N(5)-Zn(1)-N(1)	90.6(2)
N(2)-Zn(1)-N(5)	90.1(2)	O(1)-Zn(1)-Cl(3)	90.01(18)
N(2A)-Zn(1)-Cl(3)	161.3(5)	O(1)-Zn(1)-N(1)	87.5(2)
N(2A)-Zn(1)-N(1A)	83.5(6)	O(1)-Zn(1)-N(2)	101.1(2)
N(2A)-Zn(1)-N(4)	75.1(5)	O(1)-Zn(1)-N(4)	92.3(2)
N(2A)-Zn(1)-N(5)	96.2(6)	O(1)-Zn(1)-N(5)	167.8(2)

Symmetry codes: #1: -x+2, y, -z+1/2; #2: x, -y+1, z+1/2; #3: -x+2, -y+1, -z.

Table S12. Selected bond lengths (Å) and angles (°) for 5

Cd(01)-Cl(05)	2.759(6)	Cd(03)-Cl(08)	2.665(6)
Cd(01)-Cl(06)	2.529(7)	Cd(03)-Cl(09)	2.545(6)
Cd(01)-Cl(07)#1	2.717(6)	Cd(03)-Cl(0C)#1	2.802(7)
Cd(01)-Cl(0A)	2.520(5)	Cd(03)-Cl(0D)	2.569(5)
Cd(01)-N(00L)	2.363(18)	Cd(03)-N(00S)	2.37(2)
Cd(01)-N(01E)	2.41(2)	Cd(03)-N(00T)	2.384(18)
Cd(02)-Cl(05)	2.572(5)	Cd(04)-Cl(08)	2.518(5)
Cd(02)-Cl(06)#2	2.783(7)	Cd(04)-Cl(09)#2	2.702(7)
Cd(02)-Cl(07)	2.524(6)	Cd(04)-Cl(0C)	2.563(7)
Cd(02)-Cl(0A)	2.646(6)	Cd(04)-Cl(0D)	2.790(6)
Cd(02)-N(00J)	2.33(2)	Cd(04)-N(00H)	2.340(19)
Cd(02)-N(00U)	2.372(18)	Cd(04)-N(00R)	2.393(18)
Cl(05)-Cd(02)-Cl(06)#2	98.8(2)	N(00J)-Cd(02)-Cl(06)#2	84.8(5)
Cl(05)-Cd(02)-Cl(0A)	84.11(18)	N(00J)-Cd(02)-Cl(07)	156.2(5)
Cl(06)-Cd(01)-Cl(05)	100.2(2)	N(00J)-Cd(02)-Cl(0A)	94.7(5)
Cl(06)-Cd(01)-Cl(07)#1	84.9(2)	N(00J)-Cd(02)-N(00U)	70.4(7)
Cl(07)#1-Cd(01)-Cl(05)	172.82(17)	N(00L)-Cd(01)-Cl(05)	85.7(6)
Cl(07)-Cd(02)-Cl(05)	108.2(2)	N(00L)-Cd(01)-Cl(06)	90.5(6)
Cl(07)-Cd(02)-Cl(06)#2	83.6(2)	N(00L)-Cd(01)-Cl(07)#1	99.5(6)
Cl(07)-Cd(02)-Cl(0A)	95.8(2)	N(00L)-Cd(01)-Cl(0A)	162.9(6)
Cl(08)-Cd(03)-Cl(0C)#1	177.84(18)	N(00L)-Cd(01)-N(01E)	69.7(7)
Cl(08)-Cd(04)-Cl(09)#2	90.15(19)	N(00R)-Cd(04)-Cl(08)	161.0(6)
Cl(08)-Cd(04)-Cl(0C)	105.0(3)	N(00R)-Cd(04)-Cl(09)#2	99.1(5)
Cl(08)-Cd(04)-Cl(0D)	83.03(17)	N(00R)-Cd(04)-Cl(0C)	92.3(6)
Cl(09)#2-Cd(04)-Cl(0D)	172.44(18)	N(00R)-Cd(04)-Cl(0D)	86.5(5)
Cl(09)-Cd(03)-Cl(08)	95.2(2)	N(00S)-Cd(03)-Cl(08)	94.6(5)
Cl(09)-Cd(03)-Cl(0C)#1	83.7(2)	N(00S)-Cd(03)-Cl(09)	156.9(5)
Cl(09)-Cd(03)-Cl(0D)	108.3(2)	N(00S)-Cd(03)-Cl(0C)#1	85.6(5)
Cl(0A)-Cd(01)-Cl(05)	82.82(18)	N(00S)-Cd(03)-Cl(0D)	93.5(5)
Cl(0A)-Cd(01)-Cl(06)	103.9(2)	N(00S)-Cd(03)-N(00T)	70.8(6)
Cl(0A)-Cd(01)-Cl(07)#1	91.06(19)	N(00T)-Cd(03)-Cl(08)	87.4(5)
Cl(0A)-Cd(02)-Cl(06)#2	177.08(19)	N(00T)-Cd(03)-Cl(09)	88.8(5)
Cl(0C)-Cd(04)-Cl(09)#2	85.5(2)	N(00T)-Cd(03)-Cl(0C)#1	90.7(5)
Cl(0C)-Cd(04)-Cl(0D)	99.4(2)	N(00T)-Cd(03)-Cl(0D)	161.7(5)
Cl(0D)-Cd(03)-Cl(08)	84.63(18)	N(00U)-Cd(02)-Cl(05)	161.5(6)
Cl(0D)-Cd(03)-Cl(0C)#1	97.5(2)	N(00U)-Cd(02)-Cl(06)#2	90.1(6)
N(00H)-Cd(04)-Cl(08)	96.2(4)	N(00U)-Cd(02)-Cl(07)	88.9(6)
N(00H)-Cd(04)-Cl(09)#2	81.0(5)	N(00U)-Cd(02)-Cl(0A)	87.1(5)
N(00H)-Cd(04)-Cl(0C)	154.9(5)	N(01E)-Cd(01)-Cl(05)	96.4(4)
N(00H)-Cd(04)-Cl(0D)	96.4(5)	N(01E)-Cd(01)-Cl(06)	153.1(5)

N(00H)-Cd(04)-N(00R)	69.3(6)	N(01E)-Cd(01)-Cl(07)#1	80.8(4)
N(00J)-Cd(02)-Cl(05)	94.1(4)	N(01E)-Cd(01)-Cl(0A)	99.0(5)

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

Table S13. Selected bond lengths (Å) and angles (°) for 6

Pb(1)-Cl(2A)	2.683(7)	Pb(1)-Cl(2B)#2	2.926(5)
Pb(1)-Cl(2A)#3	2.683(7)	Pb(1)-Cl(2B)#3	3.023(7)
Pb(1)-Cl(2B)	3.023(7)	Pb(1)-N(1)	2.550(14)
Pb(1)-Cl(2B)#1	2.926(5)	Pb(1)-N(1A)	2.566(14)
Cl(2A)#3-Pb(1)-Cl(2B)#	89.13(16)	Cl(2B)#3-Pb(1)-Cl(2B)	156.7(3)
Cl(2A)#3-Pb(1)-Cl(2B)#	84.68(19)	N(1)-Pb(1)-Cl(2A)	92.1(11)
Cl(2A)-Pb(1)-Cl(2A)#3	169.4(3)	N(1)-Pb(1)-Cl(2A)#3	96.8(11)
Cl(2A)-Pb(1)-Cl(2B)#1	84.68(19)	N(1)-Pb(1)-Cl(2B)#1	92.9(8)
Cl(2A)-Pb(1)-Cl(2B)#2	89.13(16)	N(1)-Pb(1)-Cl(2B)#2	158.7(8)
Cl(2A)-Pb(1)-Cl(2B)#3	166.71(15)	N(1)-Pb(1)-Cl(2B)#3	76.2(11)
Cl(2B)#1-Pb(1)-Cl(2B)	104.07(19)	N(1A)-Pb(1)-Cl(2A)#3	104.2(11)
Cl(2B)#2-Pb(1)-Cl(2B)	89.61(16)	N(1A)-Pb(1)-Cl(2B)	76.5(10)

Symmetry codes: #1: x, -y+1, z+1/2; #2: -x+2, -y+1, -z; #3: -x+2, y, -z+1/2.