Supporting Information

Synthesis and Characterization of Substituted Schiff-base Ligands and Their d^{10} Metal Complexes: Structure-induced Luminescence Tuning Behaviors and Applications in Co-sensitized Solar Cells

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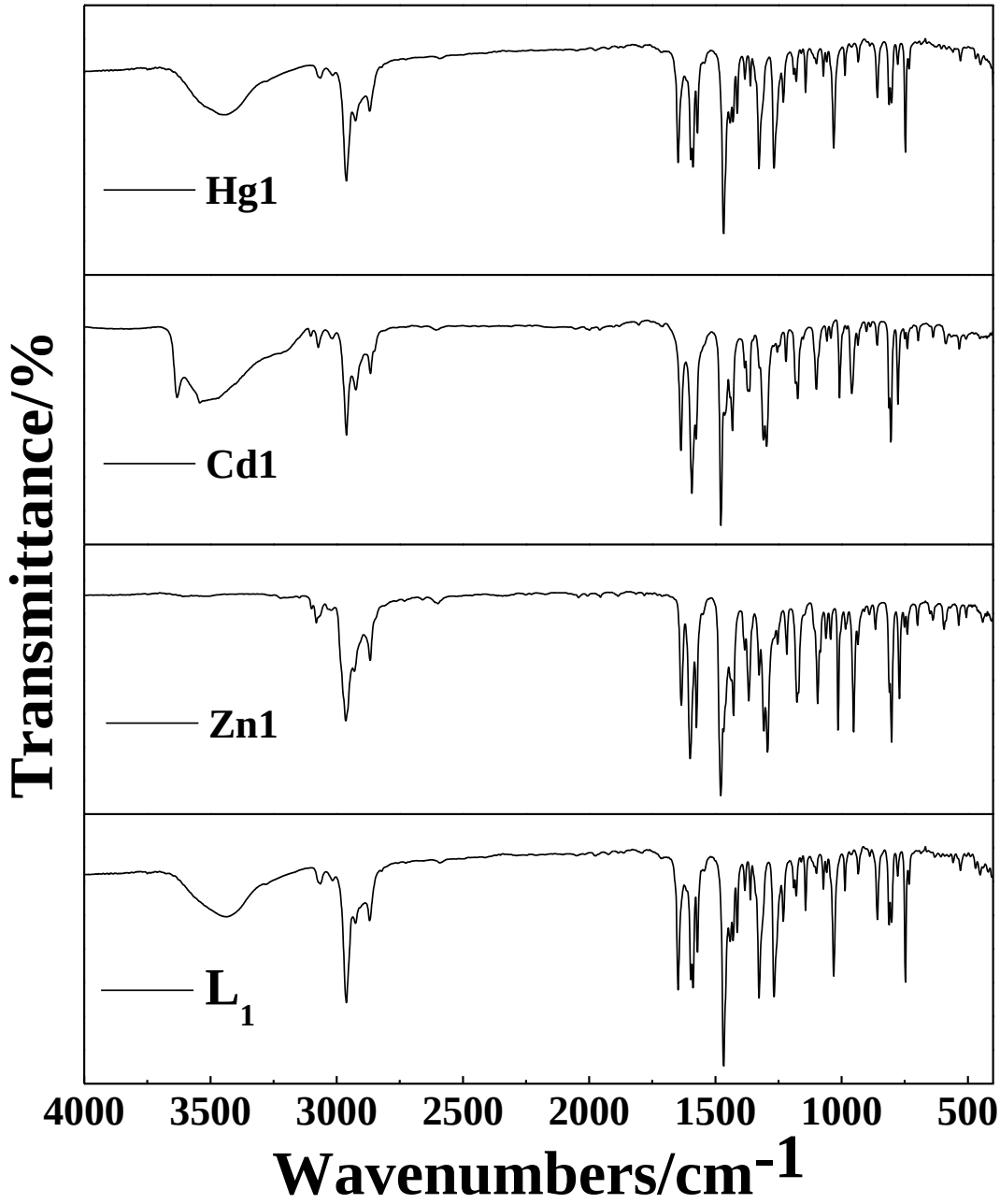

Fig. S1 Infrared spectra of free ligand $\mathbf{L_1}$ and complexes **Zn1**, **Cd1** and **Hg1** recorded from a KBr pellet.

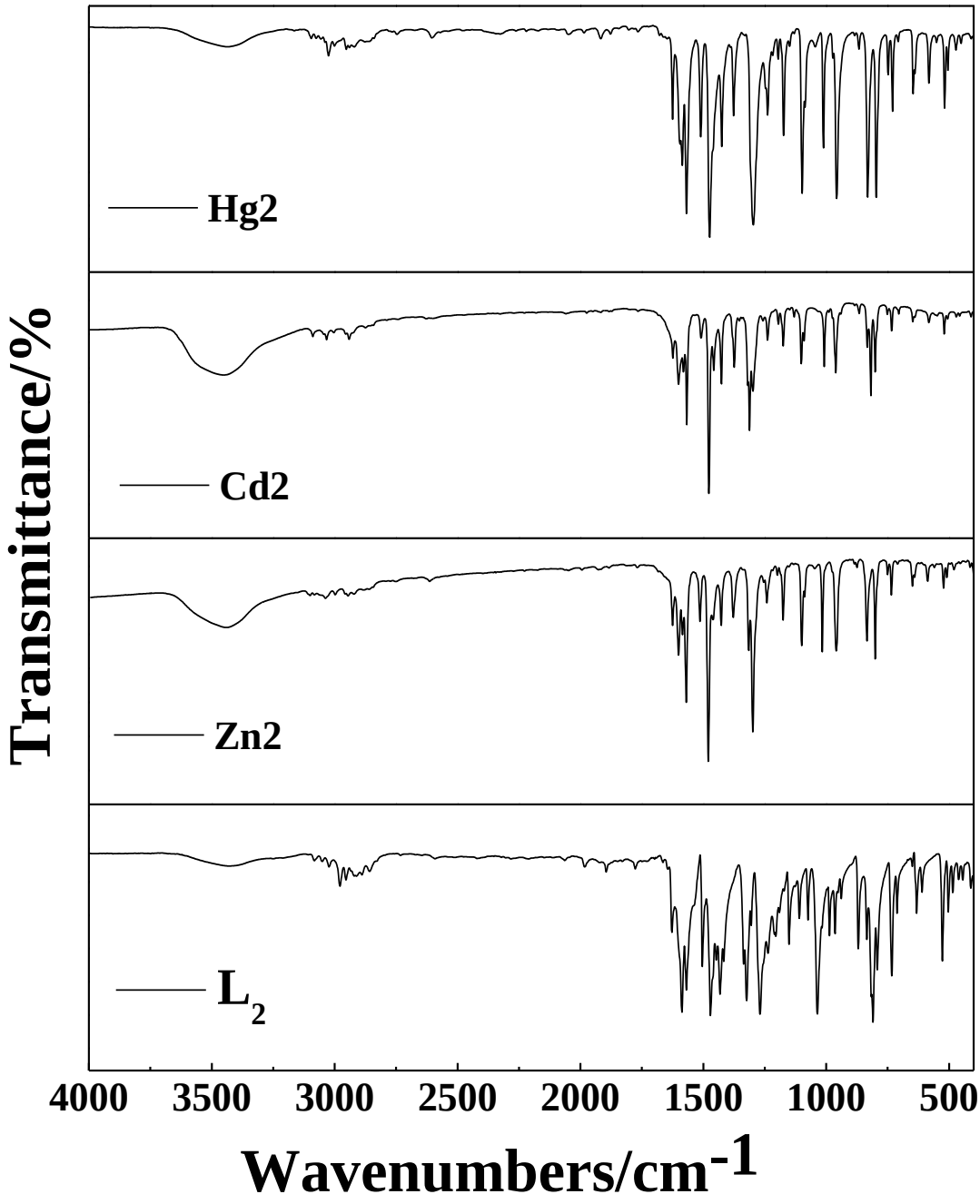

Fig. S2 Infrared spectra of free ligand **L**$_2$ and complexes **Zn2**, **Cd2** and **Hg2** recorded from a KBr pellet.

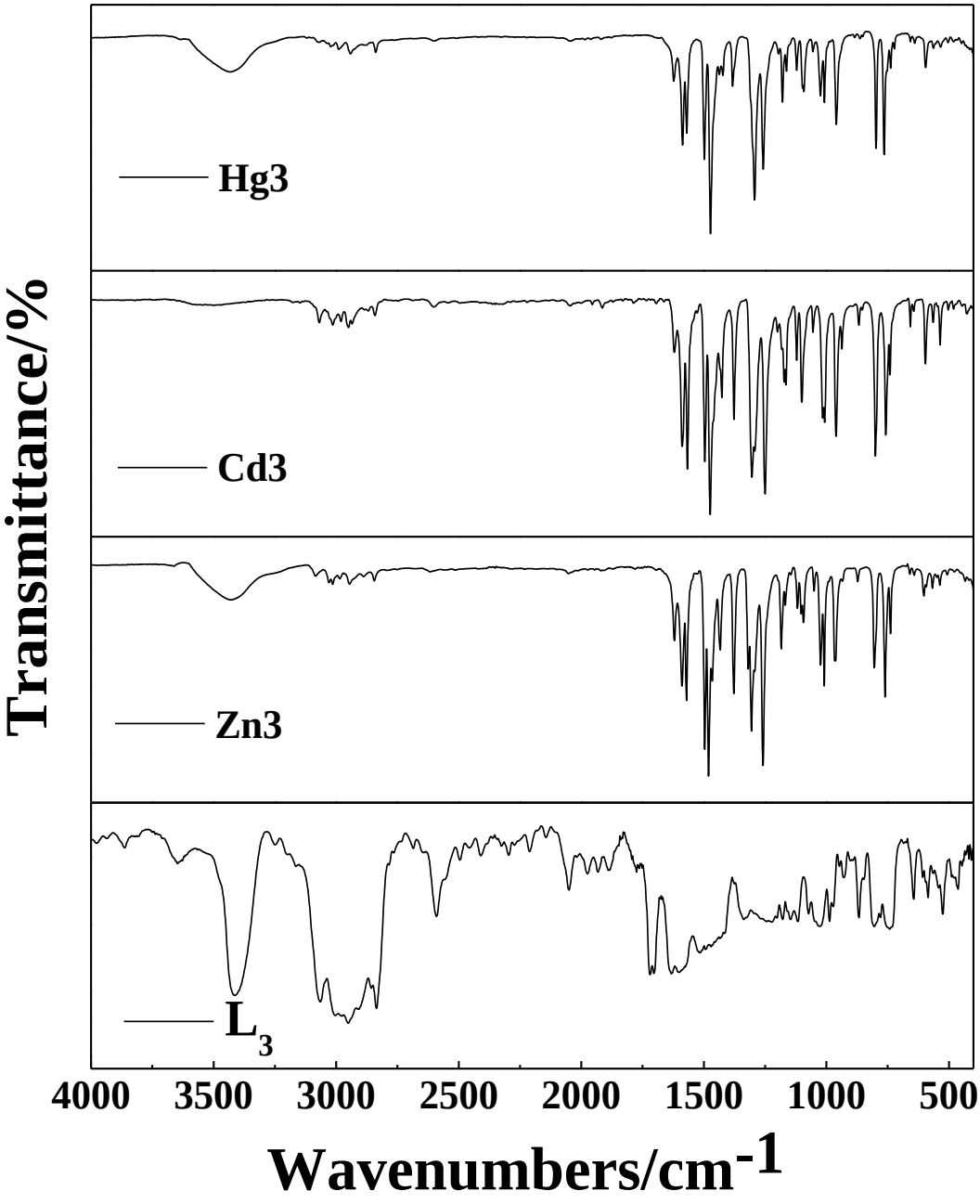

Fig. S3 Infrared spectra of free ligand **L_3** and complexes **Zn3**, **Cd3** and **Hg3** recorded from a KBr pellet.

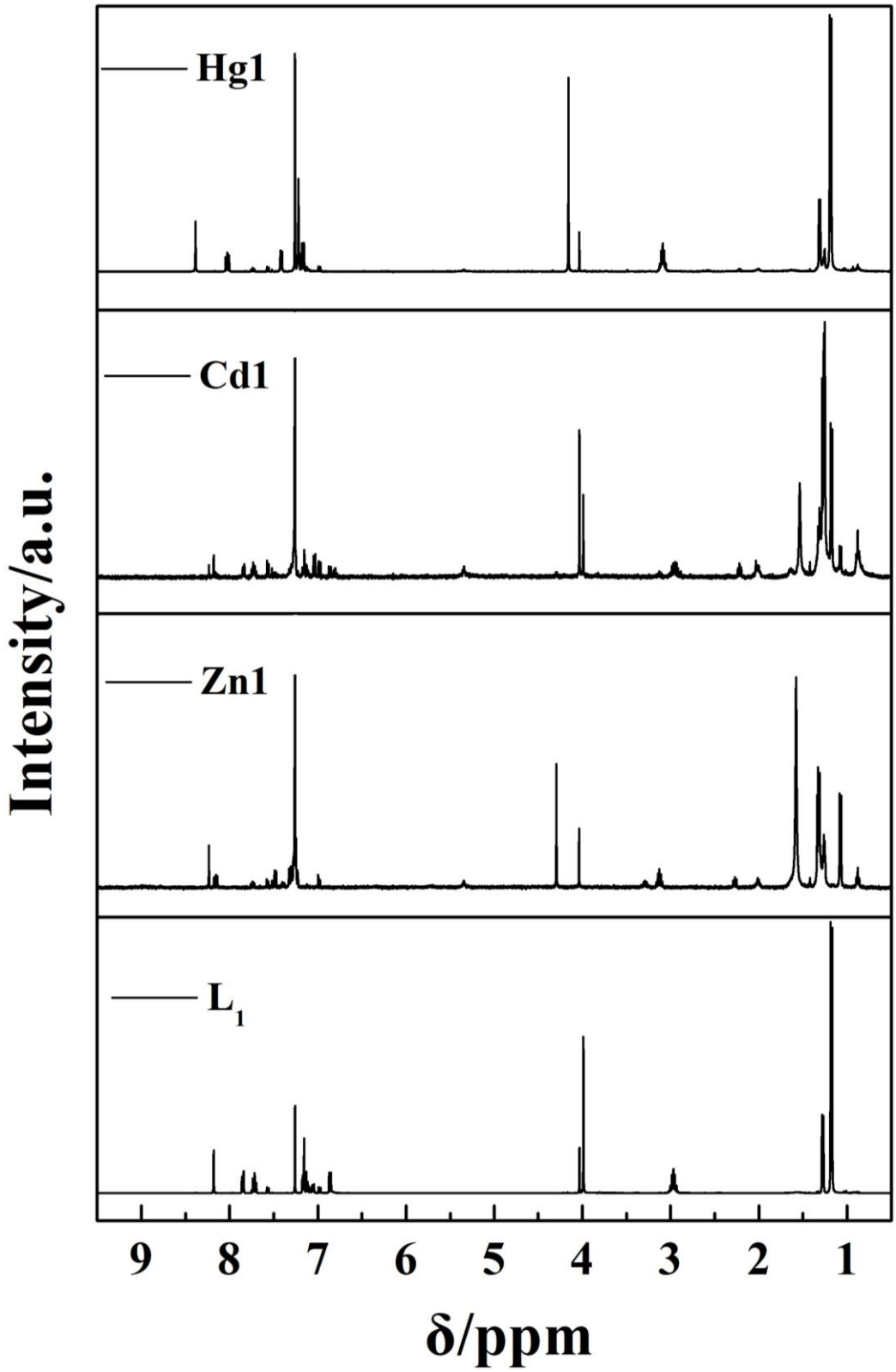

Fig. S4 ^{1}H NMR spectra of **L_1**, **Zn1**, **Cd1** and **Hg1**.

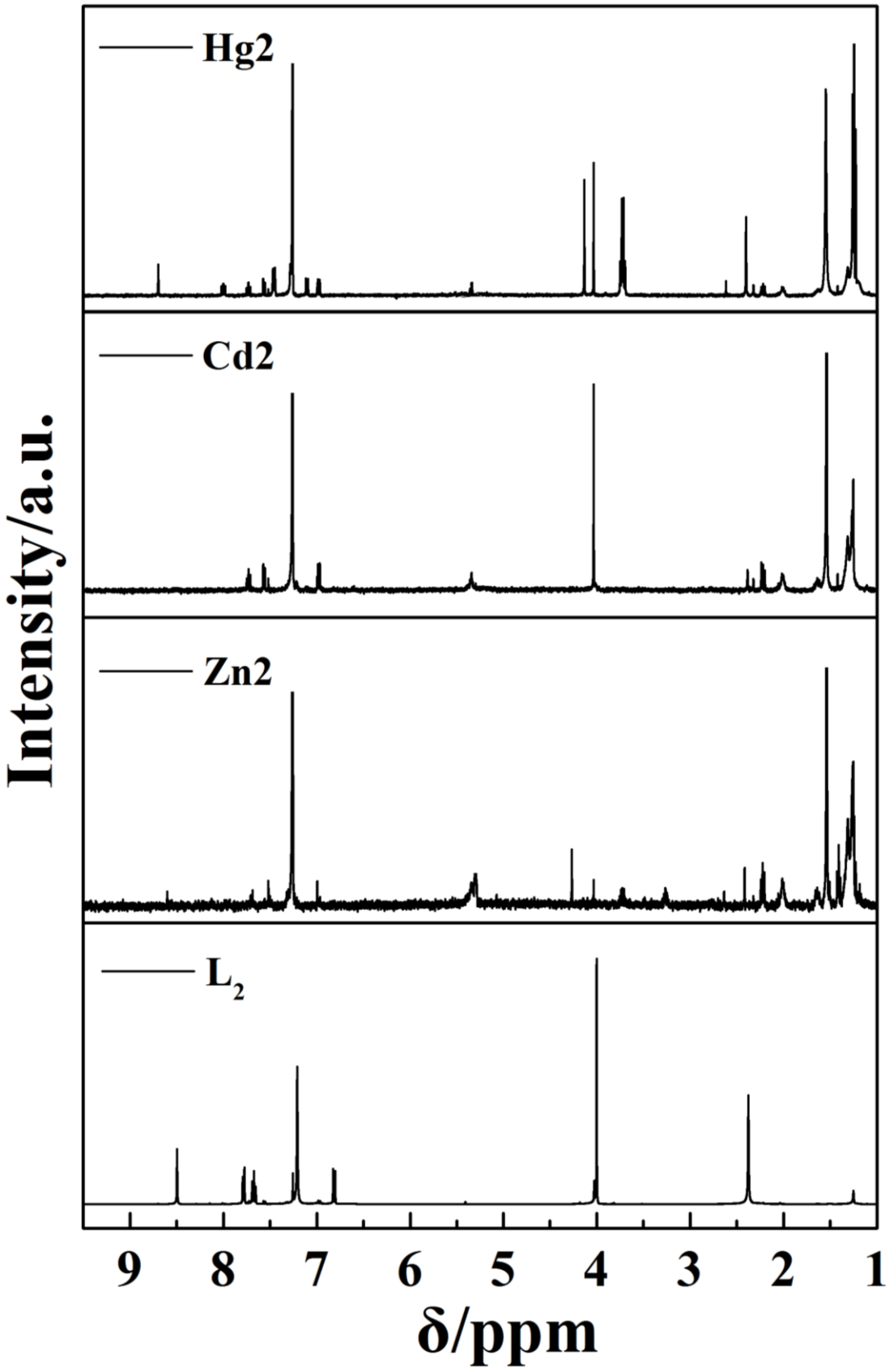

Fig. S5 ^{1}H NMR spectra of **L_2**, **Zn2**, **Cd2** and **Hg2**.

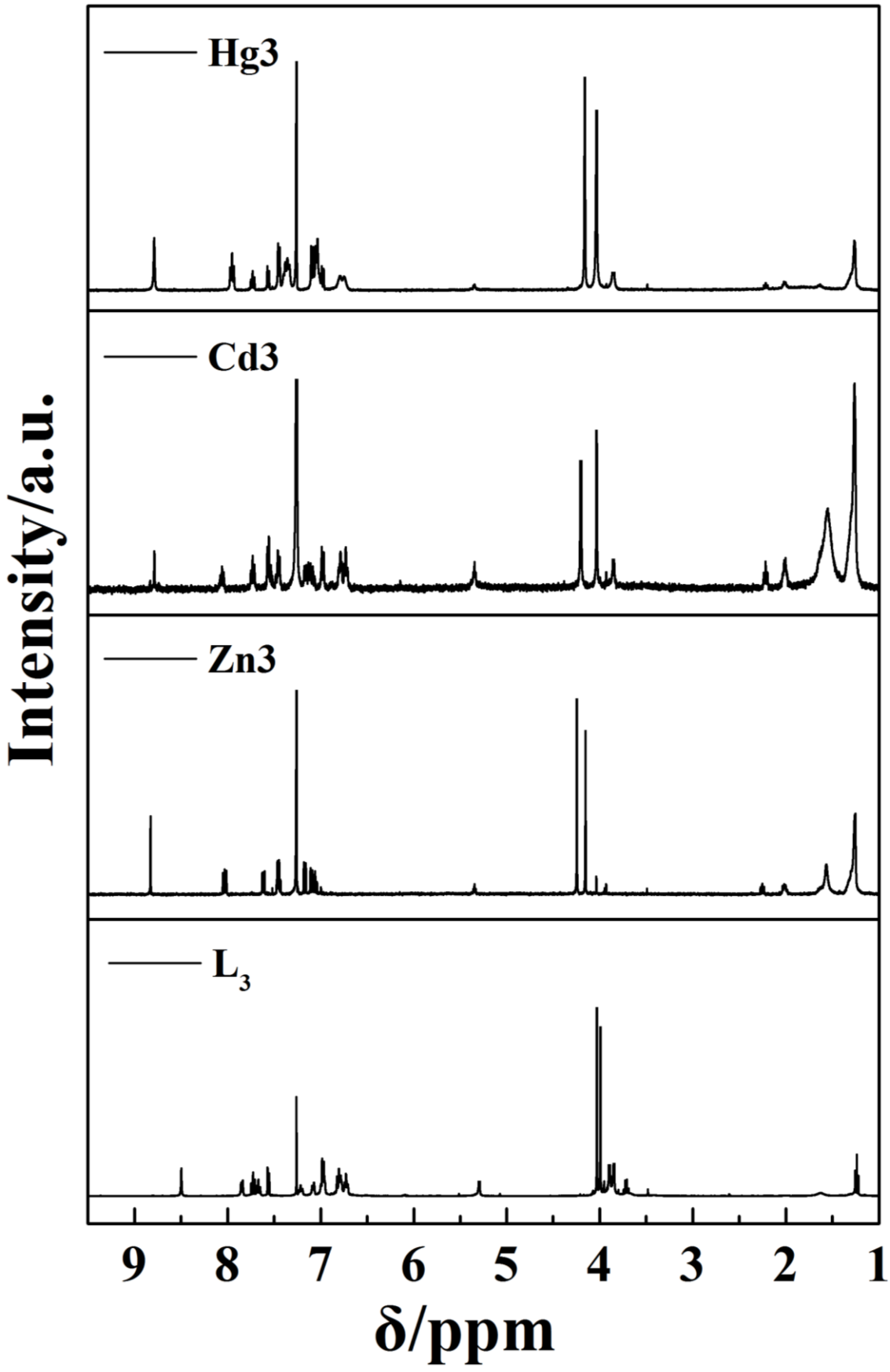

Fig. S6 ^{1}H NMR spectra of **L_3**, **Zn3**, **Cd3** and **Hg3**.

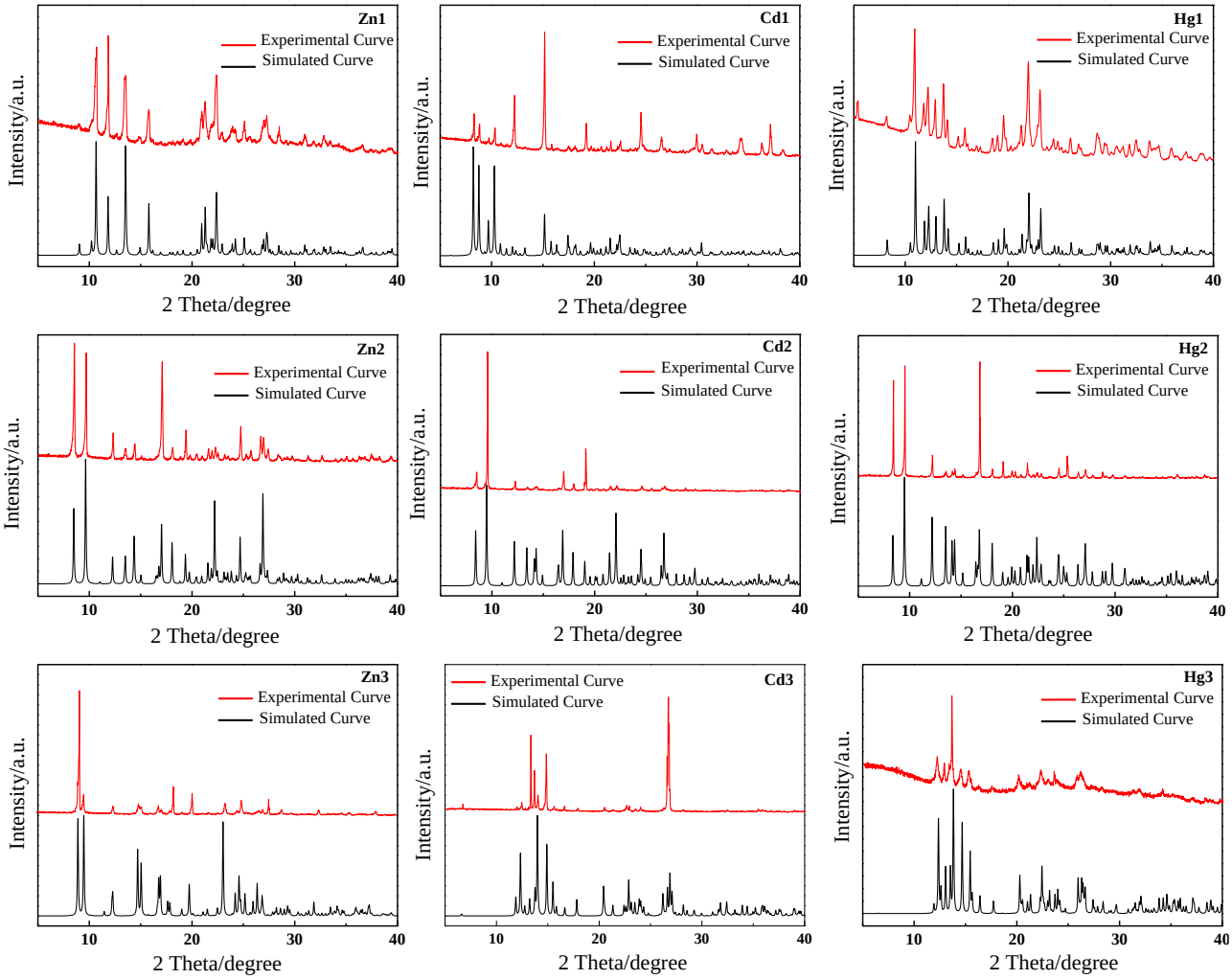

Fig. S7 Experimental (top) and simulated (bottom) PXRD patterns of complexes **Zn1**–**Zn3**, **Cd1**–**Cd3** and **Hg1**–**Hg3**.

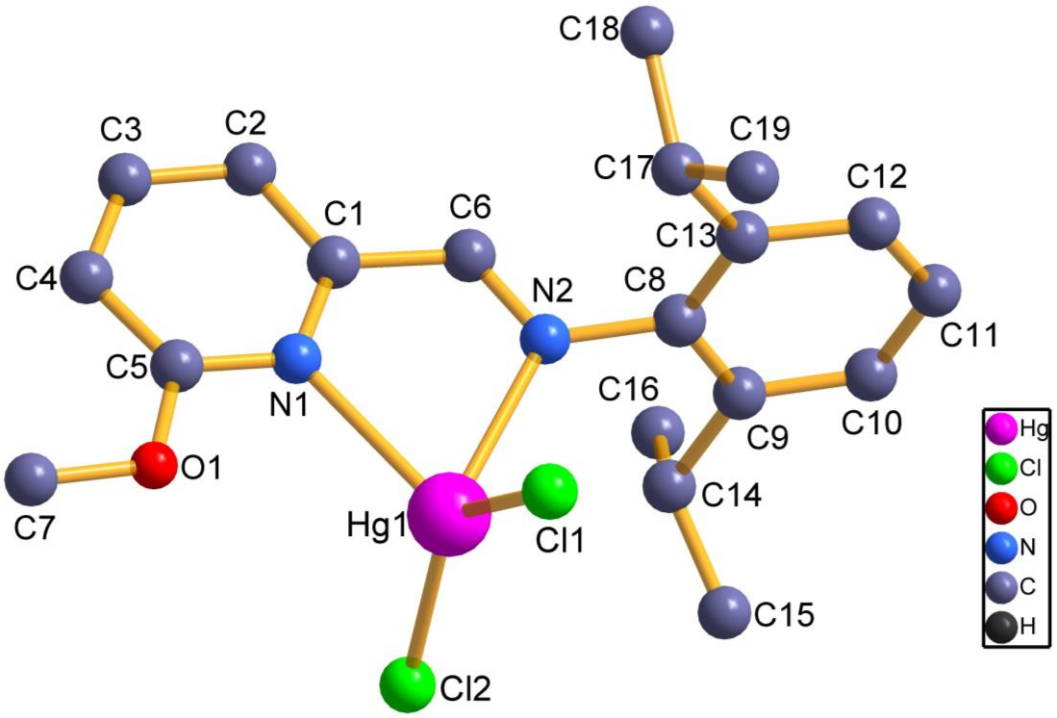

Fig. S8 The structure unit of complex **Hg1**, H atoms omitted for clarity.

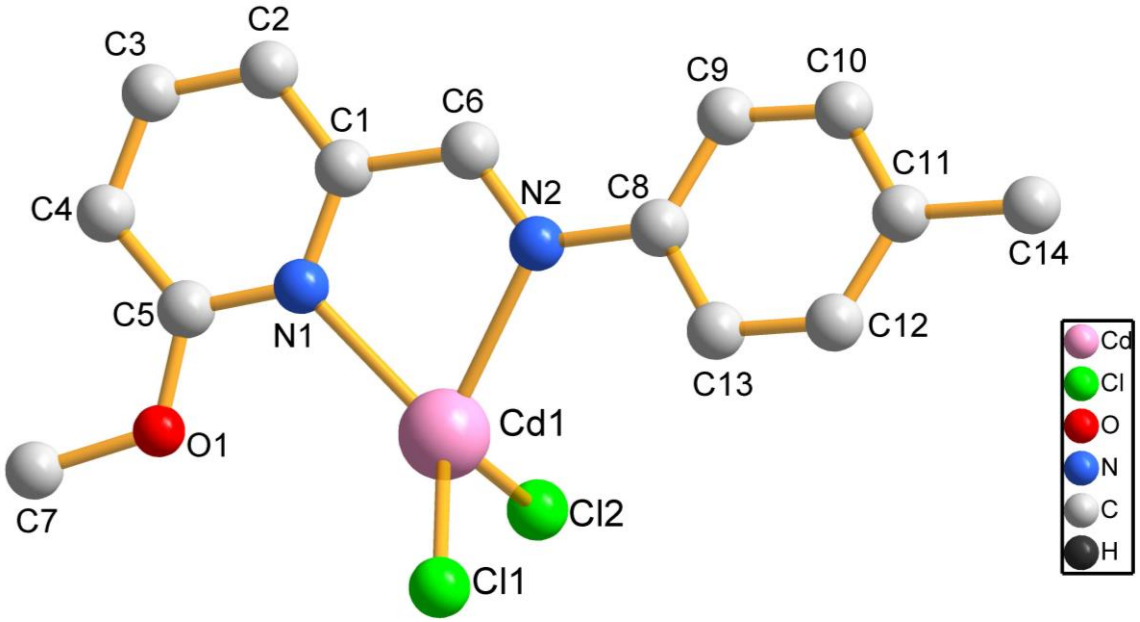

Fig. S9 The structure unit of complex **Cd2**, H atoms omitted for clarity.

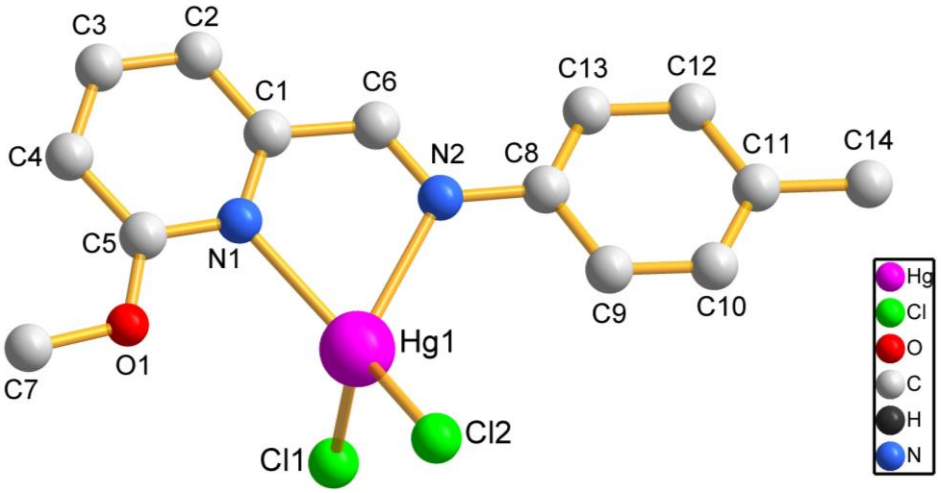

Fig. S10 The structure unit of complex **Hg2**, H atoms omitted for clarity.

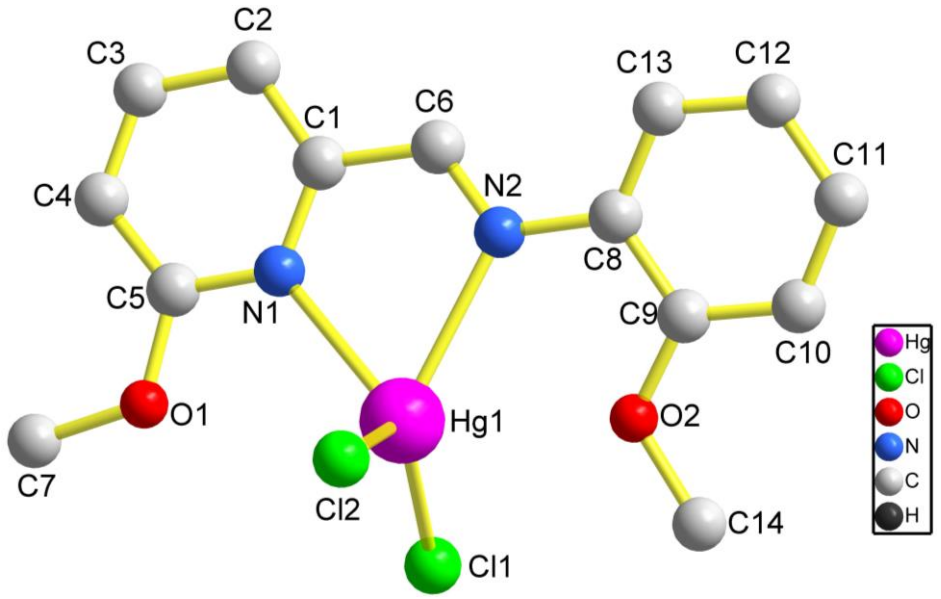

Fig. S11 The structure unit of complex **Hg3**, H atoms omitted for clarity.

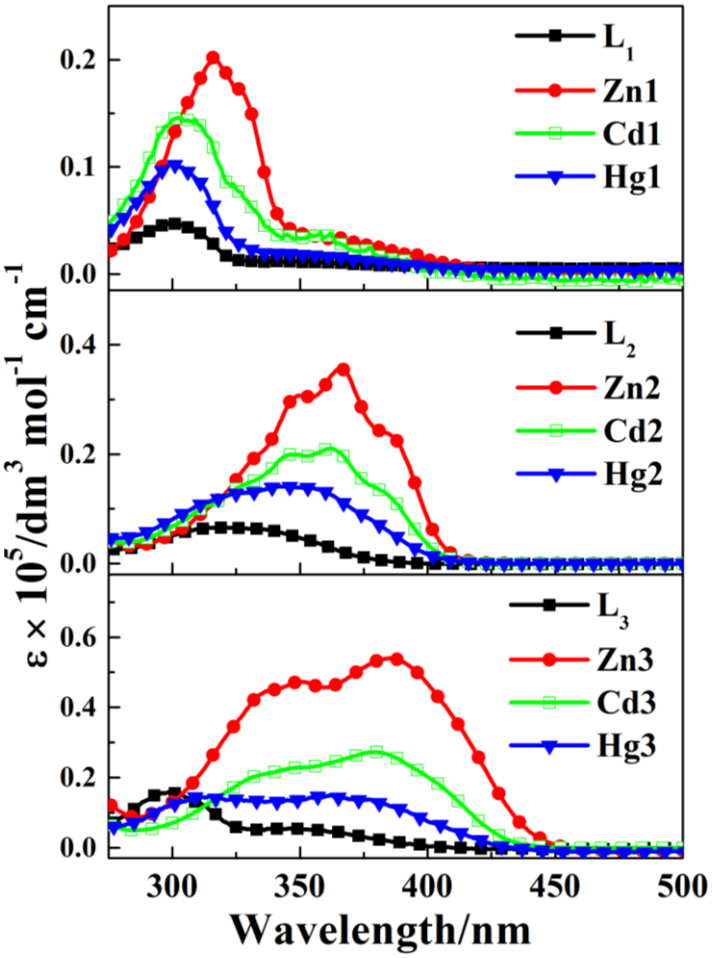

Fig. S12 UV-Vis absorption spectra of ligands **L1**–**L3** and complexes **Zn1**–**Zn3**, **Cd1**–**Cd3** and **Hg1**–**Hg3** in acetonitrile solution.

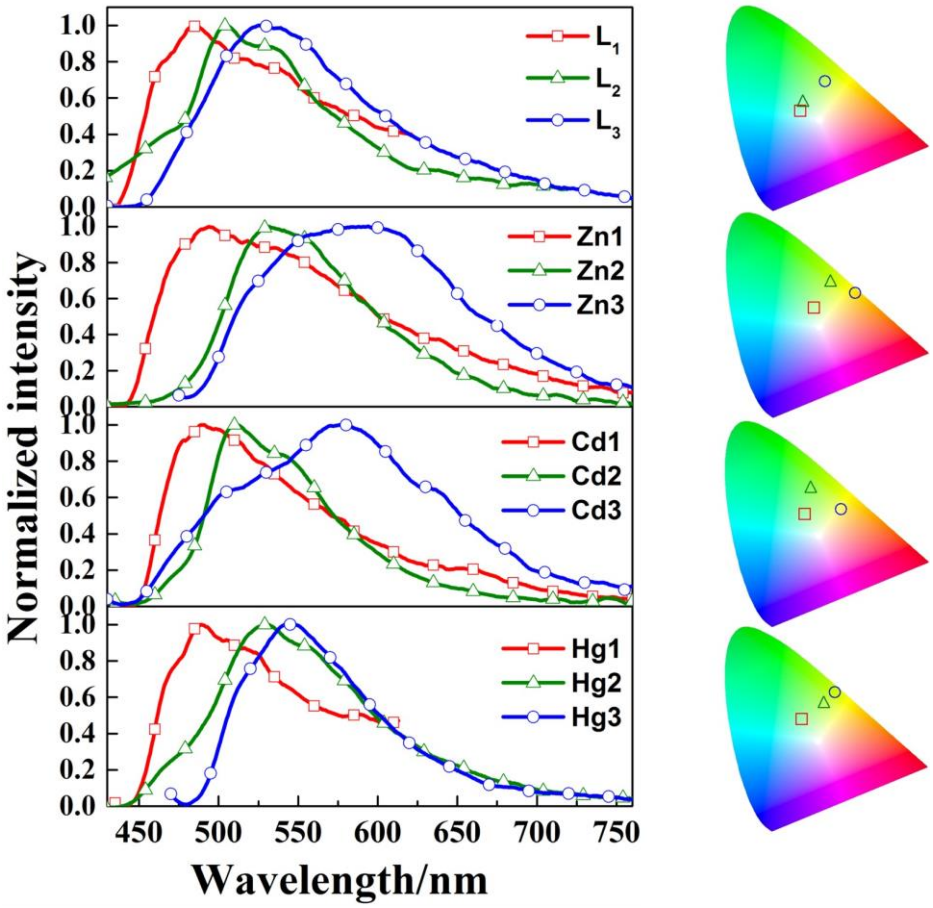

Fig. S13 Emission spectra of free ligands **L_1**–**L_3** and complexes **Zn1**–**Zn3**, **Cd1**–**Cd3** and **Hg1**–**Hg3** in acetonitrile solution at 77 K and the corresponding color coordinate diagram of emission.

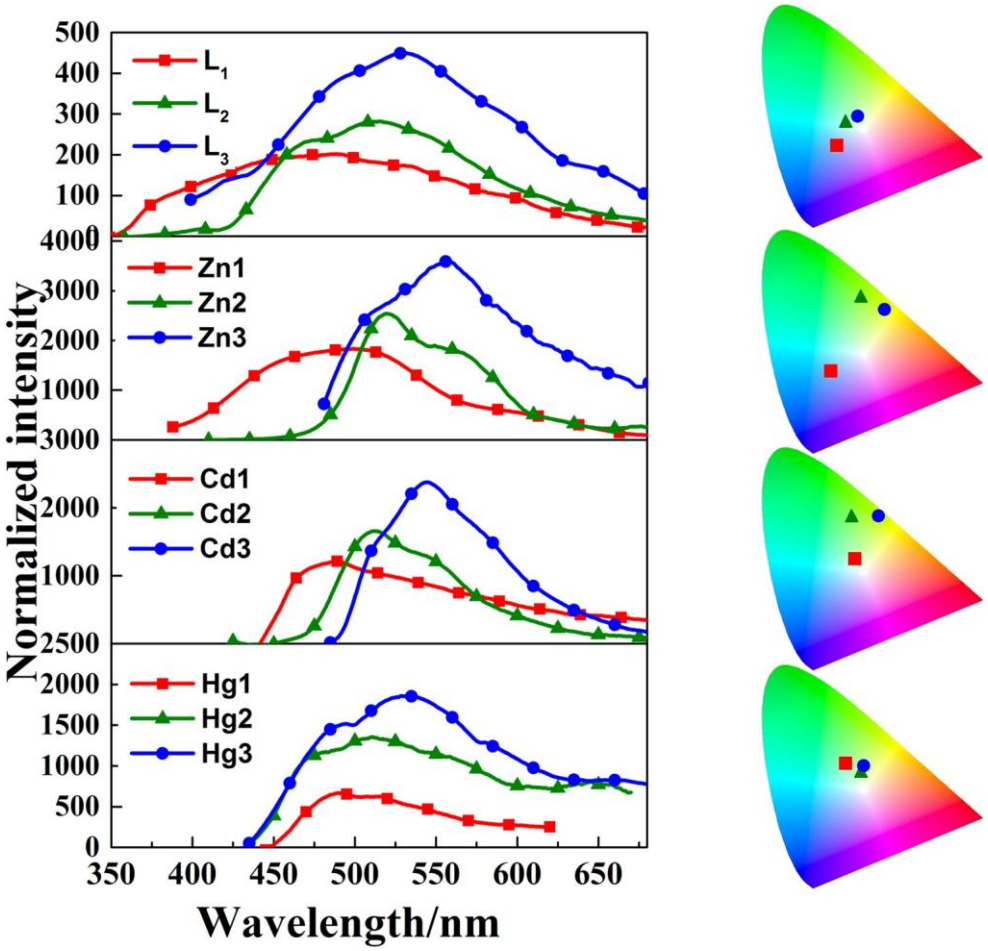

Fig. S14 Emission spectra of free ligands **L_1**–**L_3** and complexes **Zn1**–**Zn3**, **Cd1**–**Cd3** and **Hg1**–**Hg3** in solid state at 77 K at same testing condition (λ_{ex} = 365 nm, slit width: 1 nm, 1 nm) and the corresponding color coordinate diagram of emission.

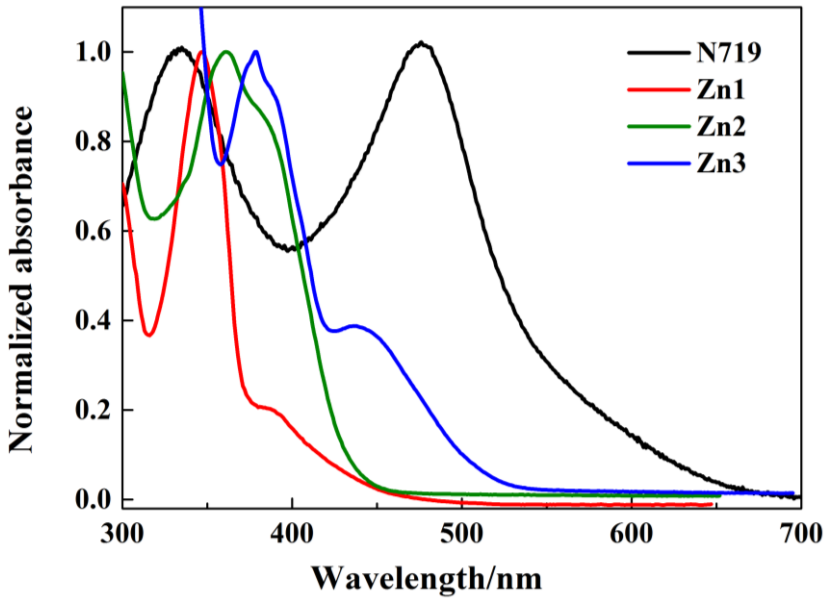

Fig. S15 UV-visible absorption spectra of complexes **Zn1**–**Zn3** and N719 in ethanol.

Table S1. Selected bond distances (Å) and angles (°) for **Zn1**–**Zn3**, **Cd2** and **Hg1**–**Hg3**.

Parameter	**Zn1**	**Hg1**	**Zn2**	**Cd2**	**Hg2**	**Zn3**	**Hg3**
M(1)-N(1)	2.068(2)	2.368(4)	2.046(5)	2.246(2)	2.262(6)	2.147(6)	2.378(5)
M(1)-N(2)	2.1137(19)	2.477(4)	2.112(6)	2.329(2)	2.410(8)	2.167(7)	2.439(5)
M(1)-Cl(1)	2.1746(12)	2.3475(15)	2.199(2)	2.3695(8)	2.450(2)	2.285(2)	2.3816(19)
M(1)-Cl(2)	2.2021(11)	2.3440(17)	2.226(2)	2.4073(9)	2.362(2)	2.260(2)	2.4080(18)
N(2)-C(6)	1.269(3)	1.246(6)	1.279(9)	1.276(4)	1.282(9)	1.294(10)	1.276(8)
N(1)-M(1)-N(2)	78.89(8)	69.00(12)	80.4(2)	73.01(9)	71.6(3)	78.6(2)	69.36(18)
N(1)-M(1)-Cl(1)	118.55(7)	115.76(11)	122.06(19)	127.86(7)	108.11(18)	101.86(19)	110.18(15)
N(2)-M(1)-Cl(1)	117.79(6)	101.47(10)	116.14(18)	117.64(6)	104.66(16)	114.58(18)	125.57(13)
N(1)-M(1)-Cl(2)	112.09(7)	105.75(11)	111.08(19)	110.95(7)	134.32(18)	110.8(2)	106.86(14)
N(2)-M(1)-Cl(2)	105.28(6)	109.52(10)	109.13(17)	107.65(7)	118.90(16)	120.46(19)	104.80(13)
Cl(1)-M(1)-Cl(2)	117.57(5)	134.86(8)	113.47(8)	112.61(3)	110.80(8)	119.78(8)	124.98(8)
C(5)-N(1)-M(1)	126.66(19)	123.2(3)	129.4(5)	124.2(2)	120.6(7)	128.3(5)	123.5(5)
C(1)-N(1)-M(1)	113.71(16)	117.3(3)	112.2(5)	115.3(2)	117.5(5)	112.2(5)	116.7(4)
C(6)-N(2)-M(1)	112.99(17)	114.6(3)	110.4(5)	113.0(2)	112.1(6)	113.0(5)	114.3(4)
C(8)-N(2)-M(1)	126.06(14)	125.4(3)	127.4(4)	125.10(17)	125.9(5)	125.1(5)	123.9(4)

Table S2. Selected bond distances (Å) and angles (°) for **Cd1**.

Parameter		Parameter		Parameter	
Cd(1)-N(1)	2.345(3)	Cd(1)-Cd(1)#1	3.7792(11)	Cd(2)-Cl(4)#2	2.5613(10)
Cd(1)-N(2)	2.396(3)	Cd(2)-N(3)	2.333(3)	Cd(2)-Cd(2)#2	3.7591(9)
Cd(1)-Cl(2)	2.4119(11)	Cd(2)-N(4)	2.393(3)	Cl(1)-Cd(1)#1	2.5333(10)
Cd(1)-Cl(1)#1	2.5333(10)	Cd(2)-Cl(3)	2.4226(13)	Cl(4)-Cd(2)#2	2.5613(10)
Cd(1)-Cl(1)	2.5858(12)	Cd(2)-Cl(4)	2.5403(11)	N(2)-C(6)	1.270(4)
N(4)-C(25)	1.267(4)				
N(1)-Cd(1)-N(2)	69.93(10)	N(1)-Cd(1)-Cd(1)#1	127.47(8)	Cl(3)-Cd(2)-Cl(4)	130.88(5)
N(1)-Cd(1)-Cl(2)	103.68(9)	N(2)-Cd(1)-Cd(1)#1	108.72(7)	N(3)-Cd(2)-Cl(4)#2	157.02(8)
N(2)-Cd(1)-Cl(2)	113.05(8)	Cl(2)-Cd(1)-Cd(1)#1	122.25(4)	N(4)-Cd(2)-Cl(4)#2	91.52(8)
N(1)-Cd(1)-Cl(1)#1	89.88(8)	Cl(1)#1-Cd(1)-Cd(1)#1	42.96(2)	Cl(3)-Cd(2)-Cl(4)#2	102.20(4)
N(2)-Cd(1)-Cl(1)#1	119.03(8)	Cl(1)-Cd(1)-Cd(1)#1	41.88(3)	Cl(4)-Cd(2)-Cl(4)#2	85.07(4)
Cl(2)-Cd(1)-Cl(1)#1	127.69(5)	N(3)-Cd(2)-N(4)	69.89(10)	N(3)-Cd(2)-Cd(2)#2	130.41(7)
N(1)-Cd(1)-Cl(1)	153.03(8)	N(3)-Cd(2)-Cl(3)	97.06(8)	N(4)-Cd(2)-Cd(2)#2	109.61(7)
N(2)-Cd(1)-Cl(1)	89.63(7)	N(4)-Cd(2)-Cl(3)	110.34(8)	Cl(3)-Cd(2)-Cd(2)#2	125.89(4)
Cl(2)-Cd(1)-Cl(1)	100.42(5)	N(3)-Cd(2)-Cl(4)	91.78(8)	Cl(4)-Cd(2)-Cd(2)#2	42.75(2)
Cl(1)#1-Cd(1)-Cl(1)	84.84(4)	N(4)-Cd(2)-Cl(4)	118.03(8)	Cl(4)#2-Cd(2)-Cd(2)#2	42.32(3)
C(5)-N(1)-Cd(1)	123.7(2)	C(24)-N(3)-Cd(2)	122.6(2)		
C(1)-N(1)-Cd(1)	116.8(2)	C(20)-N(3)-Cd(2)	117.7(2)		
C(6)-N(2)-Cd(1)	115.9(2)	C(25)-N(4)-Cd(1)	115.5(2)		
C(8)-N(2)-Cd(1)	124.1(2)	C(27)-N(4)-Cd(1)	124.7(2)		

Table S3. Selected bond distances (Å) and angles (°) for **Cd3**.

Parameter		Parameter	
Cd(1)-N(1)	2.333(4)	Cd(1)-Cl(2)	2.4295(16)
Cd(1)-N(2)	2.345(4)	Cd(1)-O(2)	2.517(3)
Cd(1)-Cl(1)	2.4174(16)	N(2)-C(6)	1.290(7)
N(1)-Cd(1)-N(2)	70.97(14)	Cl(1)-Cd(1)-O(2)	89.95(9)
N(1)-Cd(1)-Cl(1)	109.88(12)	Cl(2)-Cd(1)-O(2)	98.56(10)
N(2)-Cd(1)-Cl(1)	131.68(12)	C(9)-O(2)-Cd(1)	118.1(3)
N(1)-Cd(1)-Cl(2)	107.57(13)	C(14)-O(2)-Cd(1)	123.9(3)
N(2)-Cd(1)-Cl(2)	108.72(12)	C(5)-N(1)-Cd(1)	124.4(4)
Cl(1)-Cd(1)-Cl(2)	116.02(6)	C(1)-N(1)-Cd(1)	116.1(3)
N(1)-Cd(1)-O(2)	134.56(14)	C(6)-N(2)-Cd(1)	116.2(3)
N(2)-Cd(1)-O(2)	65.62(13)	C(8)-N(2)-Cd(1)	122.0(3)

Table S4. The dihedral angels between the pyridyl ring and phenyl ring in structures of the coordinated ligand in complexes **Zn1**–**Zn3**, **Cd1**–**Cd3** and **Hg1**–**Hg3**.

	Zn1	**Cd1**	**Hg1**
Angel (pyridyl–phenyl)/ °	79.73(8)	79.58(1)	79.92(2)
	Zn2	**Cd2**	**Hg2**
Angel (pyridyl–phenyl)/ °	11.12(2)	9.91(9)	7.65(2)
	Zn3	**Cd3**	**Hg3**
Angel (pyridyl–phenyl)/ °	15.23(2)	10.53(1)	12.22(1)

Table S5. The geometrical parameters of hydrogen bonds for complexes **Zn1**–**Zn3**, **Cd1**–**Cd3** and **Hg1**–**Hg3**.

	D–H ··A	D–H/Å	H ··A/Å	D ··A/Å	D–H ··A/ °
Zn1	C16–H16A ··Cl2	0.980	2.896	3.861	168.587(2)
Cd1	C2–H2A ··Cl3	0.929	2.749	3.580	149.339(2)
	C4–H4A ··Cl1	0.931	2.915	3.495	121.771(1)
	C21–H21A ··Cl2	0.931	2.782	3.617	149.897(2)
	C23–H23A ··Cl4	0.930	2.783	3.431	127.719(1)
	C25–H25A ··Cl2	0.931	2.730	3.580	152.290(2)
Hg1	C3–H3A ··Cl2	0.930	2.941	3.704	140.358(3)
	C6–H6A ··Cl1	0.930	2.822	3.551	136.152(2)
Zn2	C6–H6A ··Cl2	0.930	2.790	3.619	149.064(8)
	C12–H12A ··Cl1	0.930	2.858	3.763	164.601(1)
	C14–H14B ··Cl2	0.960	2.841	3.779	166.081(1)
Cd2	C6–H6A ··Cl2	0.931	2.781	3.631	152.410(1)
	C9–H9A ··Cl2	0.930	2.930	3.855	173.976(1)
	C12–H12A ··Cl1	0.931	2.814	3.721	165.329(1)
Hg2	C6–H6A ··Cl1	0.930	2.738	3.611	156.750(5)
	C10–H10A ··Cl2	0.930	2.766	3.672	164.801(5)
	C13–H13A ··Cl1	0.930	2.912	3.836	173.305(5)
Zn3	C6–H6A ··Cl2	0.930	2.884	3.393	115.818(4)
	C7–H7B ··Cl2	0.960	2.906	3.568	127.124(5)
	C7–H7C ··Cl1	0.960	2.917	3.782	150.390(5)
	C14–H14C ··Cl2	0.960	2.943	3.738	141.036(5)
Cd3	C3–H3A ··Cl2	0.929	2.775	3.618	151.440(3)
	C6–H6A ··Cl1	0.930	2.862	3.711	152.423(3)
	C7–H7A ··Cl2	0.960	2.934	3.467	116.344(3)
	C12–H12A ··Cl2	0.930	2.788	3.624	150.129(3)
	C14–H14A ··Cl2	0.960	2.842	3.556	131.914(3)
Hg3	C3–H3A ··Cl2	0.929	2.816	3.647	149.625(5)
	C12–H12A ··Cl2	0.930	2.936	3.764	149.100(5)

Table S6. The geometrical parameters of π···π stacking interactions in complexes **Zn1**–**Zn3**, **Cd1**–**Cd3** and **Hg1**–**Hg3**.

Complex	Parameter	*Z* (Å)[I]	*d* (Å)[II]	*Θ* (°)[III]
Zn1	C_{g1}–C_{g1}	4.057	3.508	0.000
	C_{g2}–C_{g2}	4.192	3.696	0.000
Cd1	C_{g1}–C_{g1}	5.246	3.882	0.000
Hg1	C_{g1}–C_{g1}	4.051	3.666	0.000
	C_{g2}–C_{g2}	4.177	3.742	0.000
Zn2	C_{g1}–C_{g2}	3.837	3.513	11.126
Cd2	C_{g1}–C_{g2}	3.832	3.592	9.918
Hg2	C_{g1}–C_{g2}	3.768	3.533	7.533
Zn3	C_{g1}–C_{g2}	4.190	3.706	6.193
Cd3	C_{g1}–C_{g1}	3.690	3.574	0.000
	C_{g2}–C_{g2}	3.943	3.423	2.678
Hg3	C_{g1}–C_{g1}	3.792	3.770	0.000
	C_{g2}–C_{g2}	4.007	3.465	1.827

[I] the centroid-centroid distance; [II] the interplanar spacing; [III] the dihedral angle. Detailed annotation information of the graph setting see M. David Curtis et al.[1] C_{g1} = pyridine ring, C_{g2} = phene ring.

Table S7. The luminescence lifetimes of ligands **L_1**–**L_3** and complexes **Zn1**–**Zn3**, **Cd1**–**Cd3** and **Hg1**–**Hg3** in the solid state and acetonitrile solution at 298 K.

Complex	τ_1 (μs)	A_1 (%)	τ_2 (μs)	A_2 (%)	τ^a (μs)	Conditions
L_1	1.22	51.78	8.91	48.22	7.92	CH_3CN
	0.88	34.37	11.21	65.63	10.80	solid
Zn1	1.58	45.53	13.75	54.47	12.68	CH_3CN
	2.18	42.57	15.33	57.43	14.08	solid
Cd1	1.25	43.61	11.59	56.39	10.79	CH_3CN
	2.23	38.64	14.27	61.36	13.19	solid
Hg1	1.23	45.09	10.49	54.91	9.68	CH_3CN
	1.74	36.24	13.00	63.76	12.20	solid
L_2	1.06	79.41	8.46	20.59	6.05	CH_3CN
	1.49	35.75	12.42	64.25	11.74	solid
Zn2	1.44	41.90	12.25	58.10	11.41	CH_3CN
	3.22	47.23	18.50	52.77	16.44	solid
Cd2	1.91	47.99	14.73	52.01	13.36	CH_3CN
	2.85	43.86	18.67	56.14	16.98	solid
Hg2	1.32	43.74	10.46	56.26	9.64	CH_3CN
	3.04	45.79	16.34	54.21	14.53	solid
L_3	1.01	72.32	6.84	27.68	5.22	CH_3CN
	3.15	45.48	14.82	54.52	13.06	solid
Zn3	1.92	53.66	15.02	46.34	13.33	CH_3CN
	3.36	37.70	21.39	62.30	19.82	solid
Cd3	1.56	43.92	13.35	56.08	12.36	CH_3CN
	2.78	39.26	16.72	60.74	15.37	solid
Hg3	1.19	46.56	9.64	53.44	8.82	CH_3CN
	2.18	31.69	15.77	68.31	14.95	solid

[a] $\tau = \frac{\tau_1^2 A_1\% + \tau_2^2 A_2\%}{\tau_1 A_1\% + \tau_2 A_2\%}$

Table S8. The luminescence lifetimes of ligands **L_1**–**L_3** and complexes **Zn1**–**Zn3**, **Cd1**–**Cd3** and **Hg1**–**Hg3** in the solid state and acetonitrile solution at 77 K.

Complex	τ_1 (μs)	A_1 (%)	τ_2 (μs)	A_2 (%)	τ^a (μs)	Conditions
L_1	0.61	27.41	6.34	72.59	6.14	CH_3CN
	0.64	40.39	6.70	59.61	6.33	solid
Zn1	0.81	42.12	8.11	57.88	7.62	CH_3CN
	1.01	35.79	11.85	64.21	11.36	solid
Cd1	0.67	39.33	6.90	60.67	6.53	CH_3CN
	1.41	38.96	11.47	61.04	10.74	solid
Hg1	0.79	43.04	6.85	59.96	6.39	CH_3CN
	0.71	37.61	6.83	62.39	6.47	solid
L_2	0.78	39.13	6.31	60.87	5.90	CH_3CN
	0.74	27.80	6.55	72.20	6.31	solid
Zn2	0.85	39.31	8.91	60.69	8.44	CH_3CN
	1.05	57.12	11.88	42.88	10.74	solid
Cd2	0.84	58.49	8.15	41.51	7.22	CH_3CN
	1.02	36.37	9.45	63.63	8.96	solid
Hg2	0.91	47.88	7.31	52.12	6.65	CH_3CN
	1.11	55.09	7.93	44.91	6.93	solid
L_3	0.77	69.84	5.63	30.16	4.46	CH_3CN
	0.84	60.22	6.84	39.78	5.90	solid
Zn3	1.29	37.42	9.45	62.58	8.83	CH_3CN
	2.35	45.26	15.74	54.74	14.27	solid
Cd3	0.82	49.67	9.31	50.33	8.63	CH_3CN
	1.42	44.99	11.68	55.01	10.75	solid
Hg3	0.86	60.37	8.12	39.63	7.11	CH_3CN
	0.69	35.38	9.79	64.62	9.45	solid

[a] $\tau = \dfrac{\tau_1^2 A_1\% + \tau_2^2 A_2\%}{\tau_1 A_1\% + \tau_2 A_2\%}$

References

1 M. D. Curtis, J. Cao, J. W. Kampf, J. Am. Chem. Soc. 2004, 126, 4318.