Supporting Information

Different Conjugated System Zn(II) Schiff Base Complexes: Supramolecular Structure, Luminescent Properties and Application in PMMA-Doped Hybrid Material

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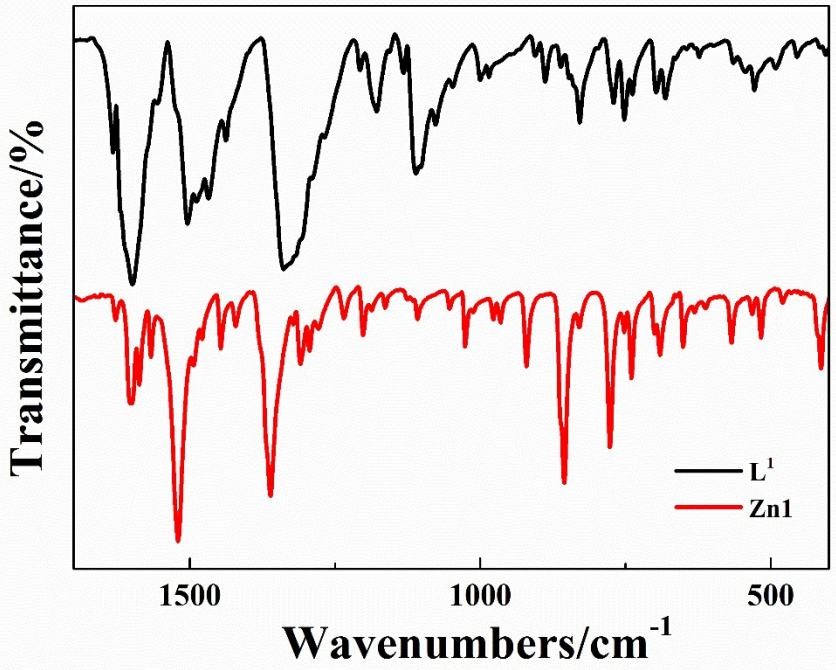

Figure S1. IR spectra of the free ligand **L**[1] and complex **Zn1** in KBr disks.

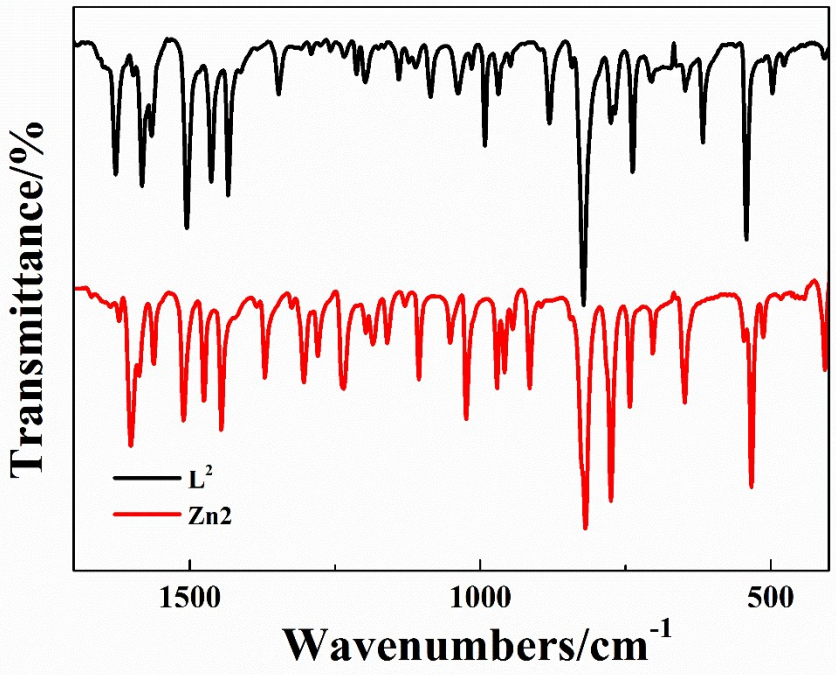

Figure S2. IR spectra of the free ligand **L**[2] and complex **Zn2** in KBr disks.

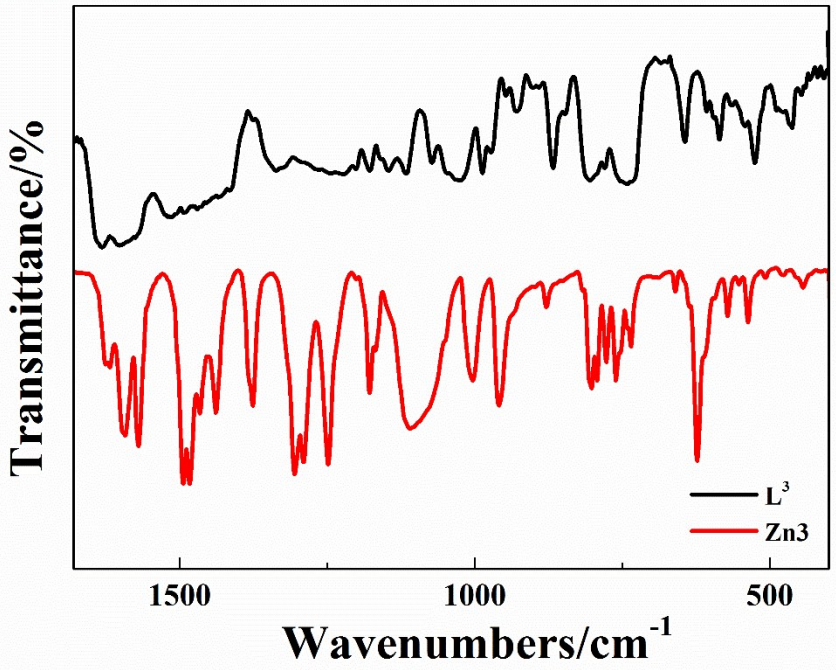

Figure S3. IR spectra of the free ligand $\mathbf{L^3}$ and complex **Zn3** in KBr disks.

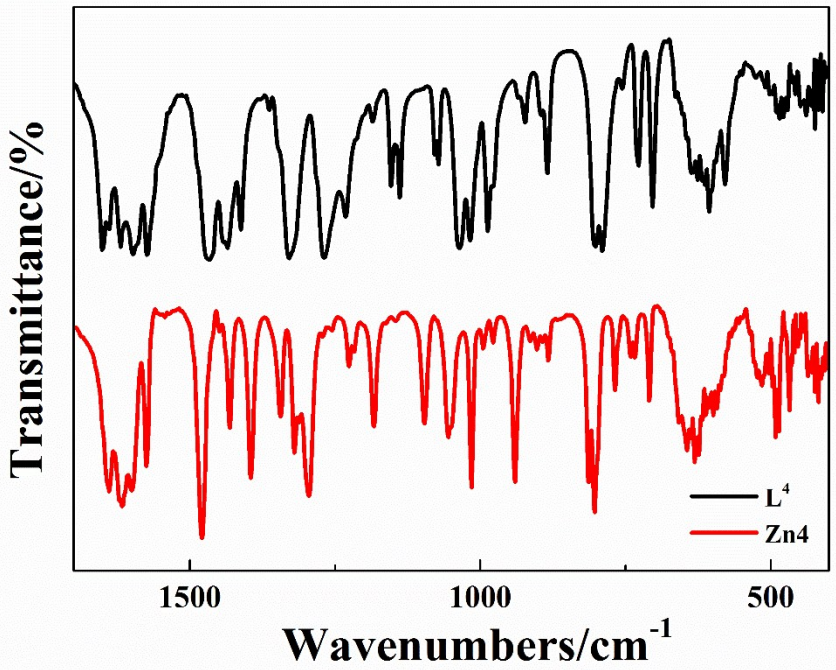

Figure S4. IR spectra of the free ligand $\mathbf{L^4}$ and complex **Zn4** in KBr disks.

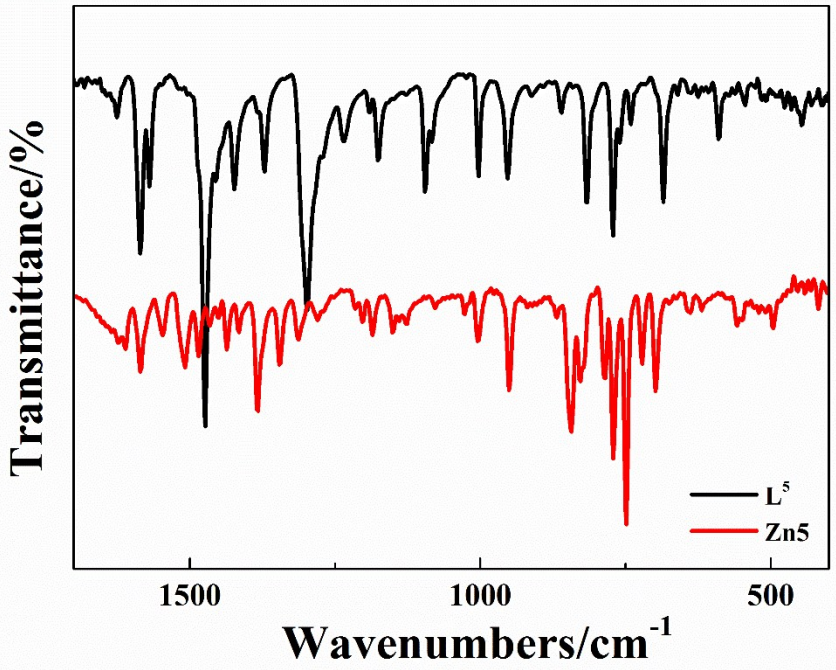

Figure S5. IR spectra of the free ligand **L**^{5} and complex **Zn5** in KBr disks.

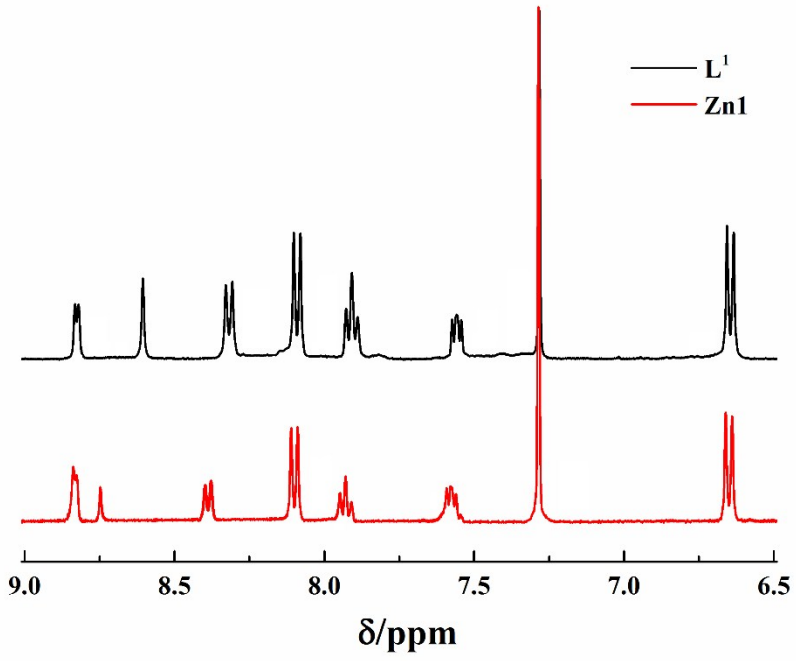

Figure S6. ^{1}H NMR spectra of the free ligand **L**^{1} and complex **Zn1** in $CDCl_3$.

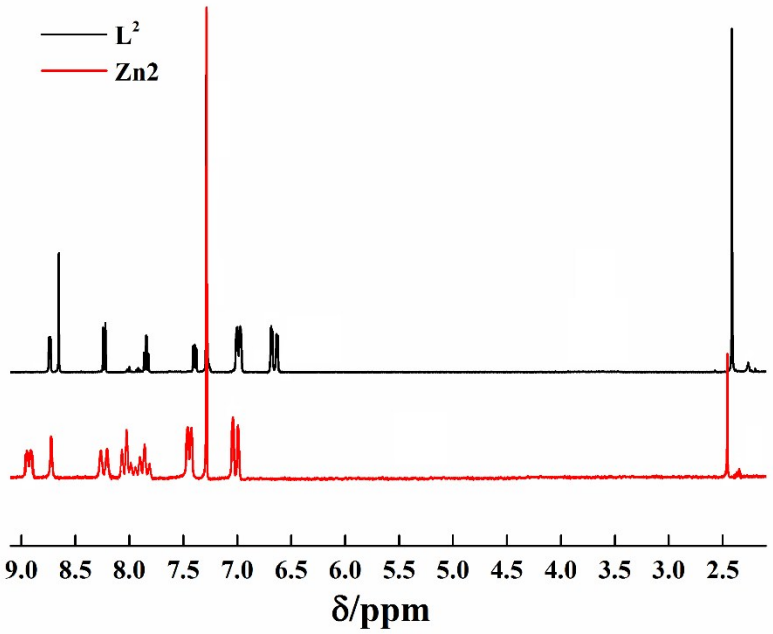

Figure S7. ^{1}H NMR spectra of the free ligand **L²** and complex **Zn2** in $CDCl_3$.

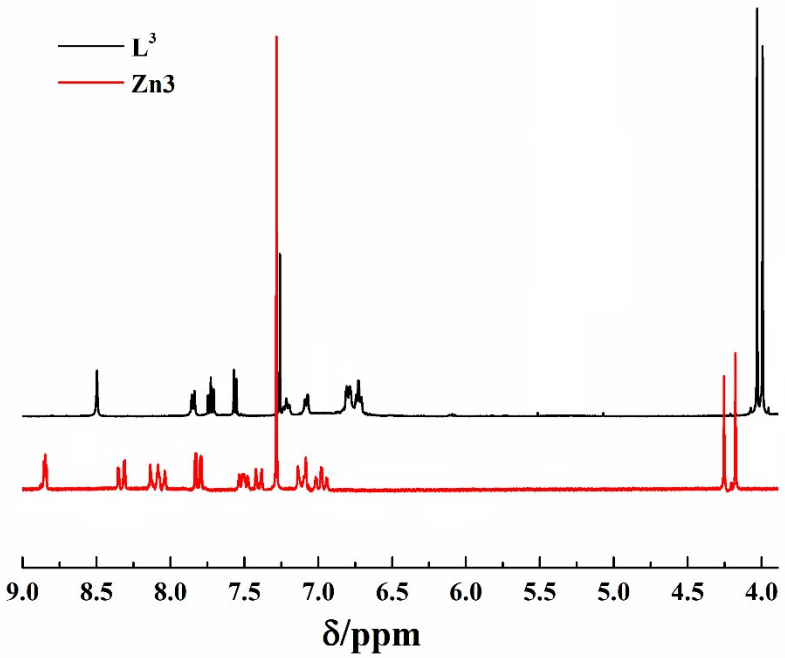

Figure S8. ^{1}H NMR spectra of the free ligand **L³** and complex **Zn3** in $CDCl_3$.

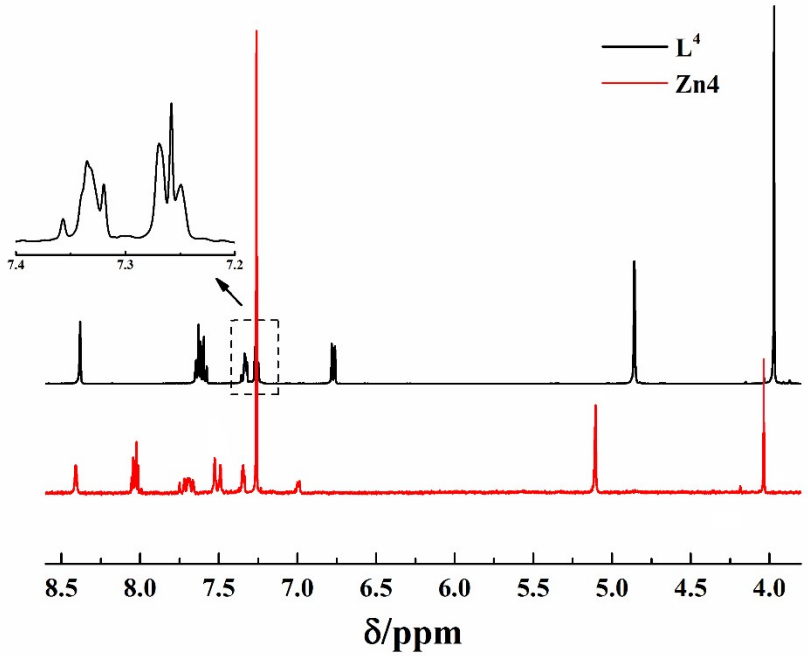

Figure S9. ^{1}H NMR spectra of the free ligand **L^{4}** and complex **Zn4** in $CDCl_3$.

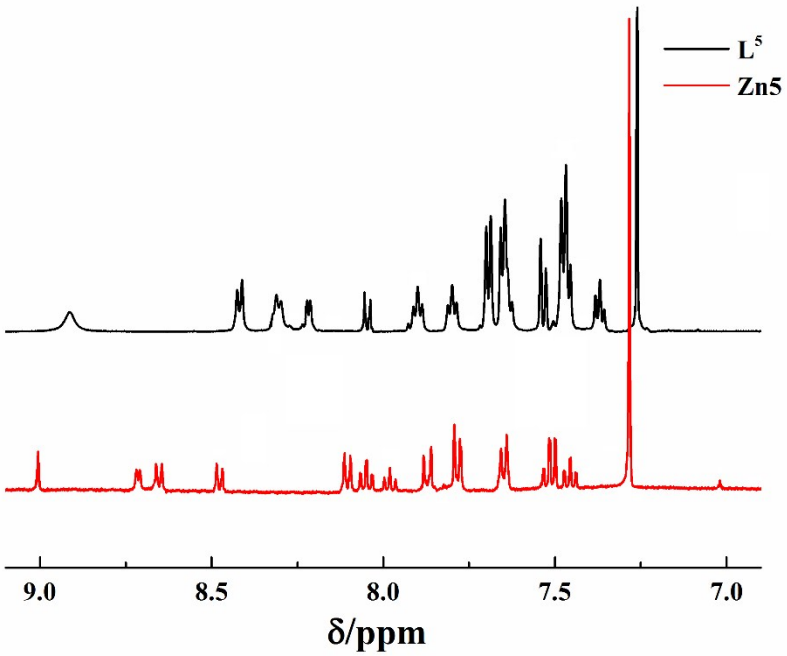

Figure S10. ^{1}H NMR spectra of the free ligand **L^{5}** and complex **Zn5** in $CDCl_3$.

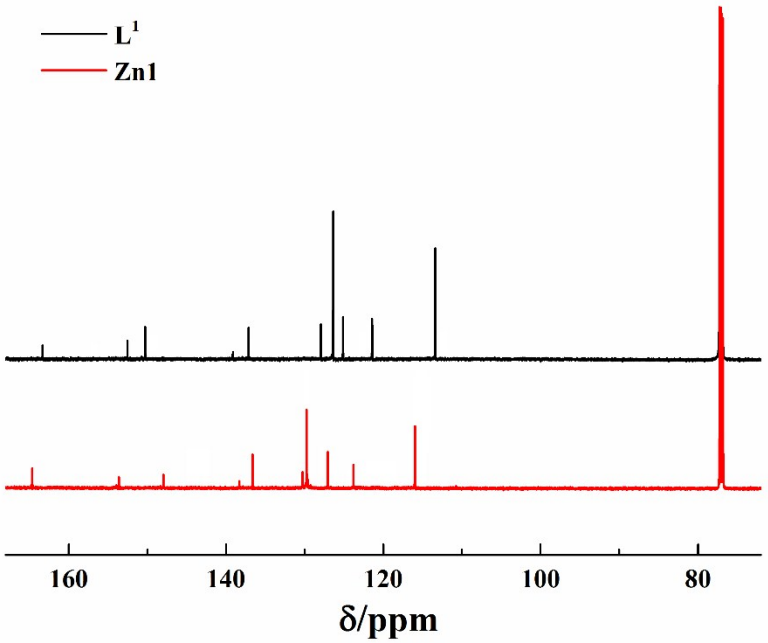

Figure S11. ^{13}C NMR spectra of the free ligand **L**^{1} and complex **Zn1** in $CDCl_3$.

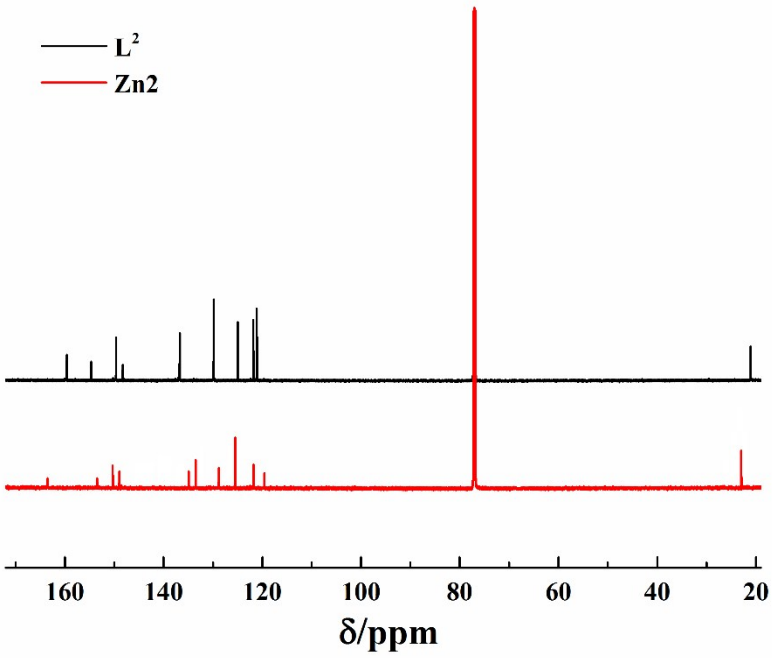

Figure S12. ^{13}C NMR spectra of the free ligand **L**^{2} and complex **Zn2** in $CDCl_3$.

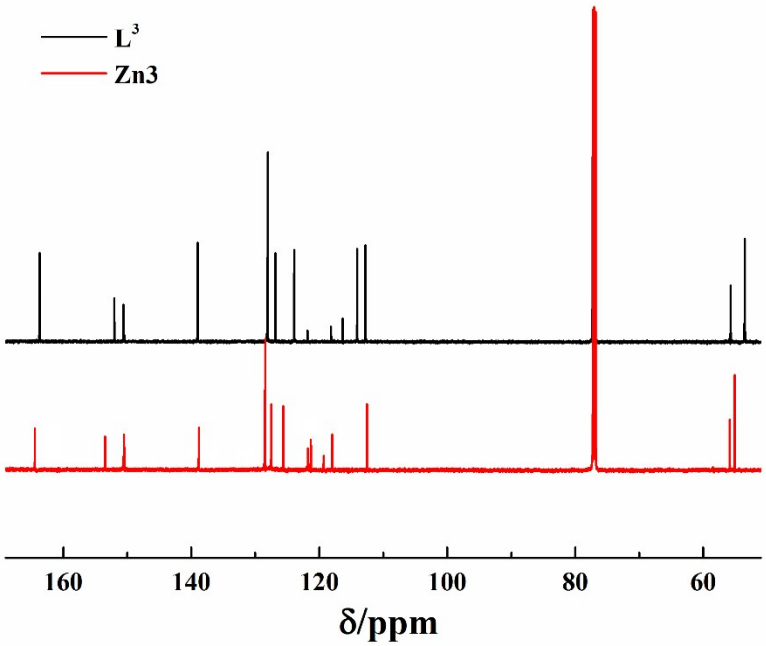

Figure S13. ^{13}C NMR spectra of the free ligand **L^3** and complex **Zn3** in $CDCl_3$.

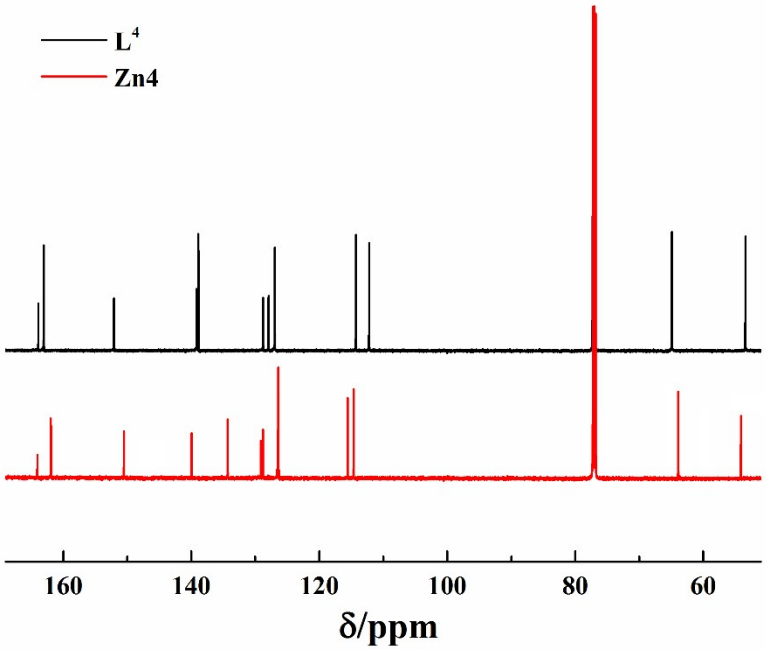

Figure S14. ^{13}C NMR spectra of the free ligand **L^4** and complex **Zn4** in $CDCl_3$.

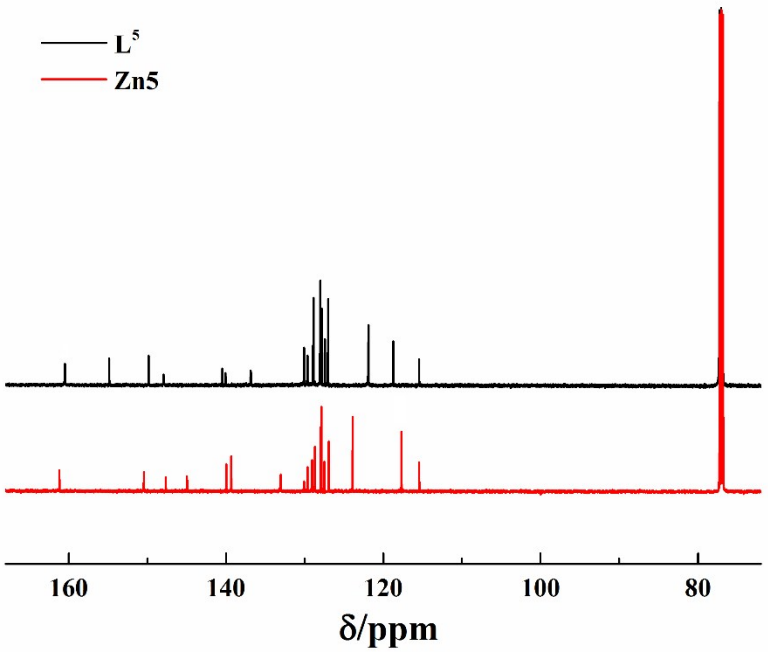

Figure S15. ^{13}C NMR spectra of the free ligand **L^5** and complex **Zn5** in $CDCl_3$.

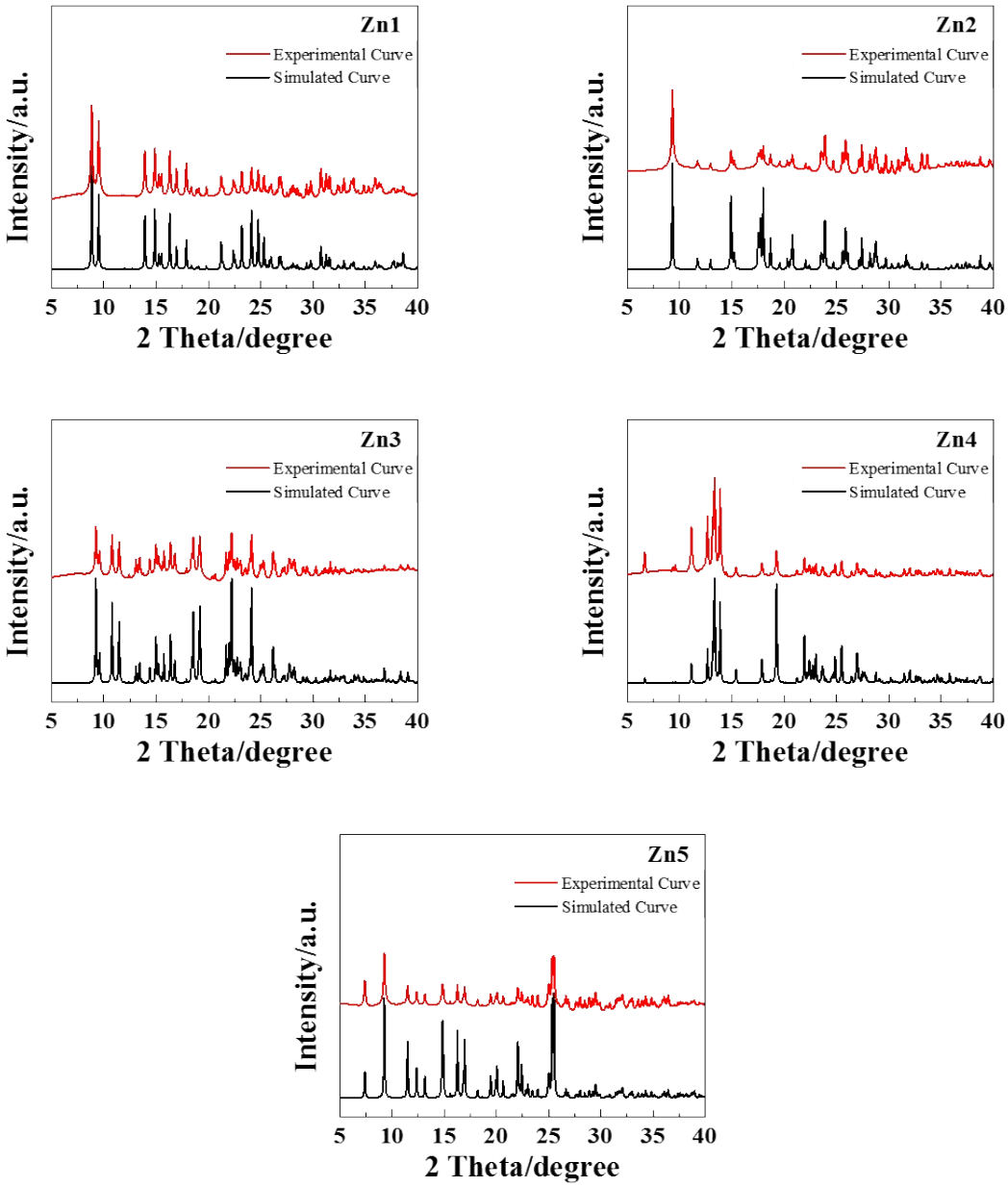

Figure S16. Experimental (top) and simulated (bottom) PXRD patterns of complexes **Zn1**–**Zn5**.

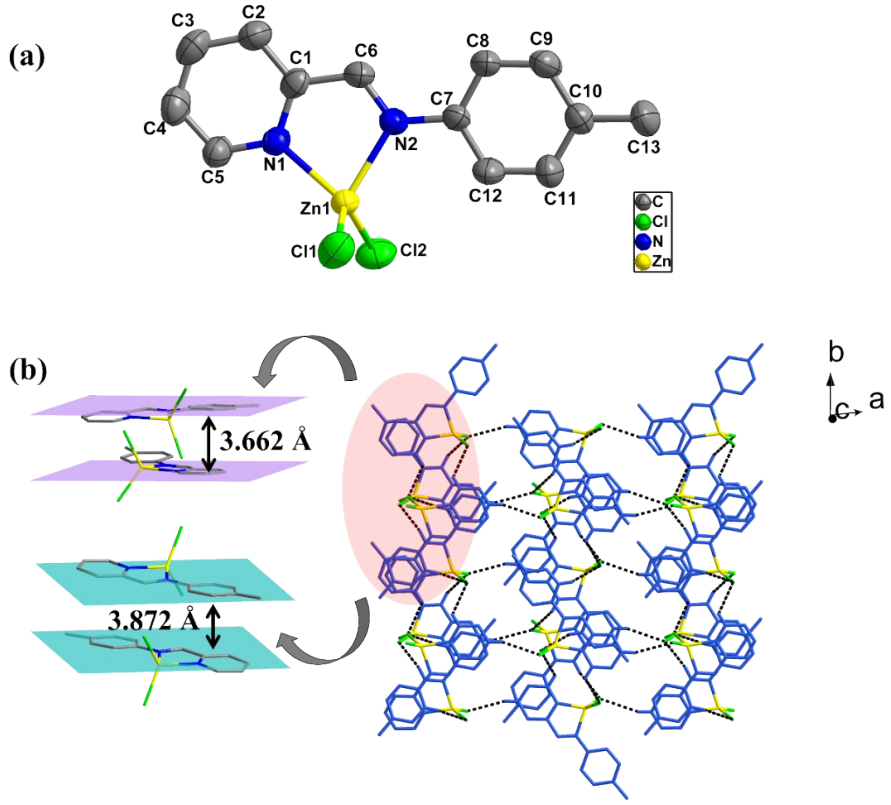

Figure S17. (a) Crystal structure of **Zn2**. Thermal ellipsoid is drawn at 50% probability. H atoms have been omitted for clarity. (b) The 3D network structure in **Zn2**. Dotted lines represent the C–H···Cl interactions.

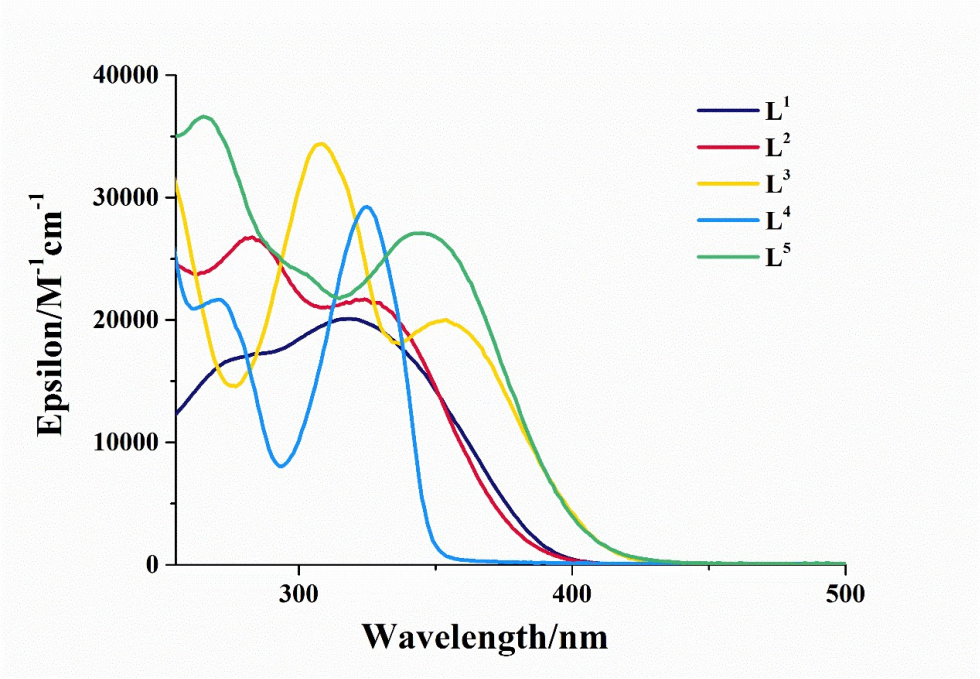

Figure S18. UV−vis absorption spectra of $\mathbf{L^1}$–$\mathbf{L^5}$ in CH_3CN at room temperature.

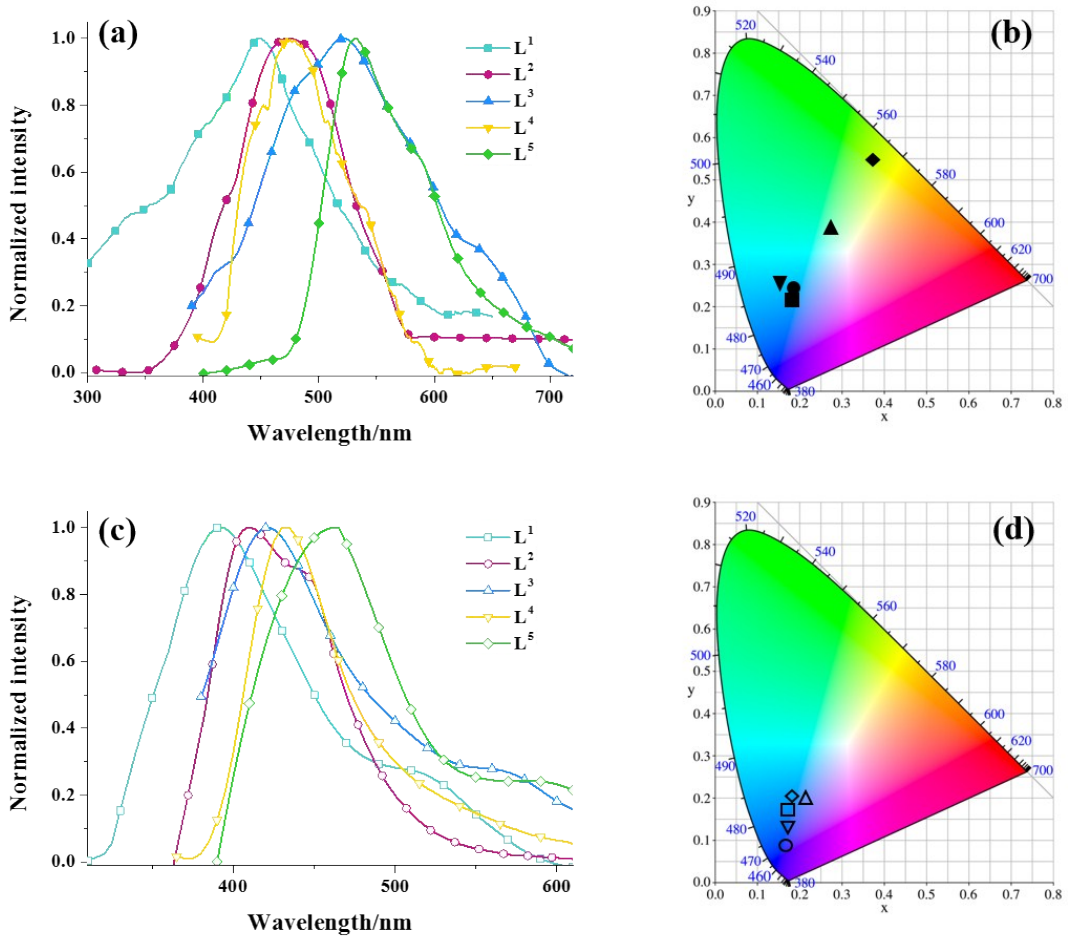

Figure S19. (a) Emission spectra of $\mathbf{L^1}$–$\mathbf{L^5}$ in the solid state and (b) CIE chromaticity diagram (1931 CIE standard). (c) Emission spectra of $\mathbf{L^1}$–$\mathbf{L^5}$ in acetonitrile solution and (d) CIE chromaticity diagram.

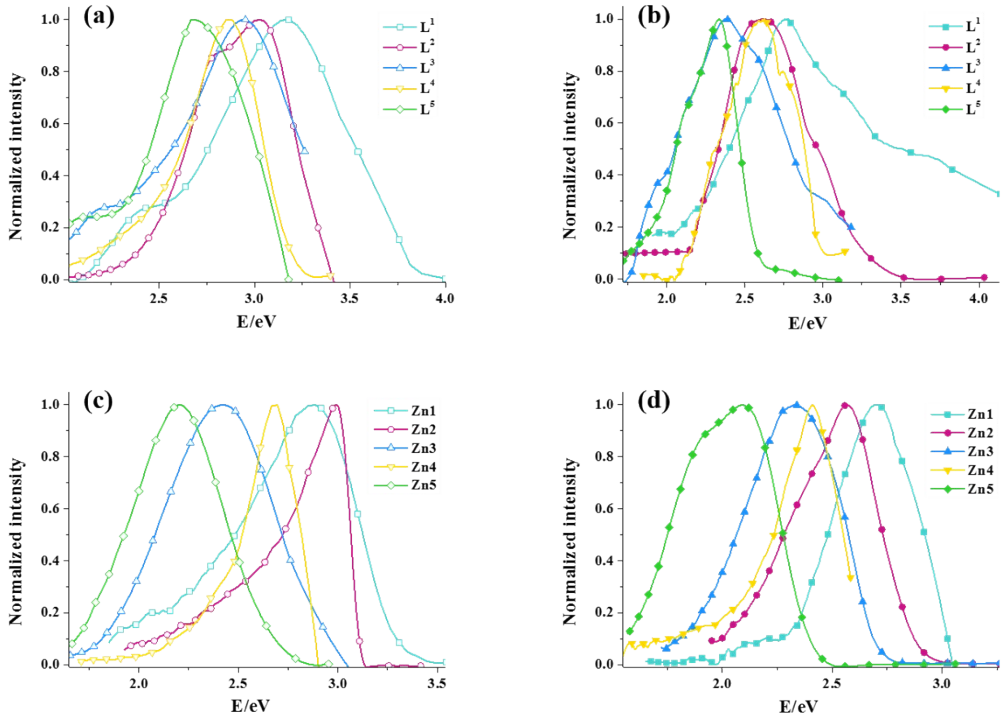

Figure S20. Emission energy spectra of $\mathbf{L^1}$–$\mathbf{L^5}$ in (a) acetonitrile solution and (b) the solid state. Emission energy spectra of **Zn1**–**Zn5** in (c) acetonitrile solution and (d) the solid state.

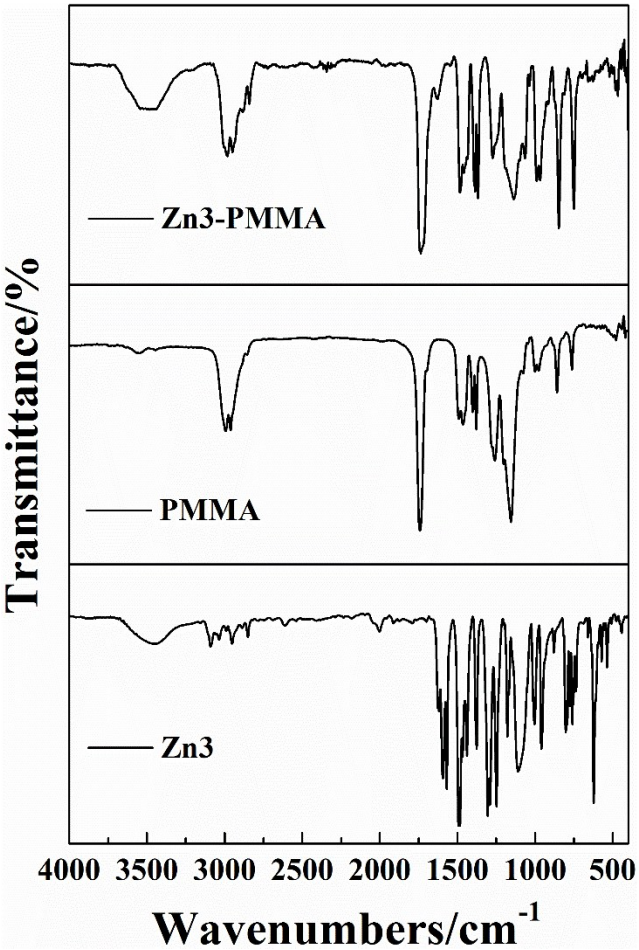

Figure S21. IR spectra of pure PMMA, **Zn3** and **Zn3**-PMMA in KBr disks.

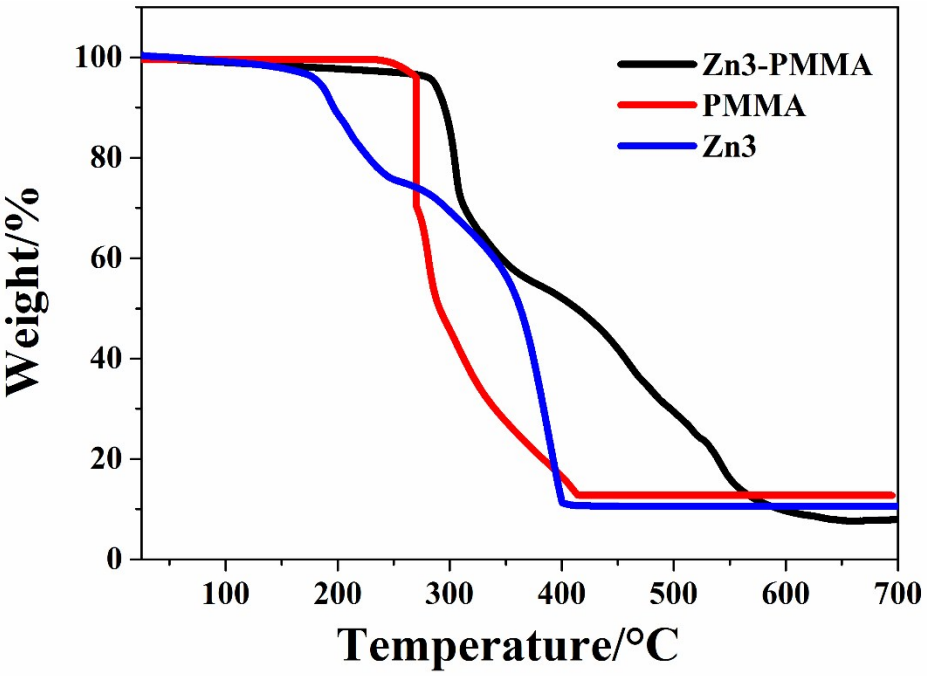

Figure S22. The comparison TG curves of pure PMMA, **Zn3** and **Zn3**-PMMA.

Table S1. Selected bond distances (Å) and angles (°) for **Zn1** and **Zn2**.

Parameter	**Zn1**	**Zn2**
Zn(1)-N(1)	2.0969(17)	2.054(5)
Zn(1)-N(2)	2.1935(17)	2.092(5)
Zn(1)-Cl(1)	2.2308(7)	2.203(2)
Zn(1)-Cl(2)	2.3320(7)	2.194(2)
N(2)-C(6)	1.279(2)	1.294(7)
N(1)-Zn(1)-N(2)	77.84(6)	80.6(2)
N(1)-Zn(1)-Cl(1)	108.91(5)	112.80(16)
N(2)-Zn(1)-Cl(1)	103.18(5)	110.94(15)
N(1)-Zn(1)-Cl(2)	132.87(5)	116.57(15)
N(2)-Zn(1)-Cl(2)	90.62(4)	111.54(14)
Cl(1)-Zn(1)-Cl(2)	118.22(3)	118.25(8)
C(5)-N(1)-Zn(1)	128.03(15)	128.7(5)
C(1)-N(1)-Zn(1)	114.26(12)	112.5(4)
C(6)-N(2)-Zn(1)	112.17(14)	111.4(4)
C(7)-N(2)-Zn(1)	127.88(12)	125.0(4)

Table S2. Selected bond distances (Å) and angles (°) for **Zn3**–**Zn5**.

Zn3			
Parameter		Parameter	
Zn(1)-N(1)	2.062(6)	N(4)-Zn(1)-O(2)	86.93(19)
Zn(1)-N(2)	2.075(6)	N(1)-Zn(1)-O(2)	147.2(2)
Zn(1)-N(3)	2.088(5)	N(2)-Zn(1)-O(2)	70.3(2)
Zn(1)-N(4)	2.053(5)	N(3)-Zn(1)-O(2)	101.81(19)
Zn(1)-O(2)	2.471(5)	O(4)-Zn(1)-O(2)	79.41(17)
Zn(1)-O(4)	2.316(4)	C(9)-O(2)-Zn(1)	110.5(4)
N(2)-C(6)	1.255(9)	C(14)-O(2)-Zn(1)	132.5(5)
N(4)-C(20)	1.286(8)	C(23)-O(4)-Zn(1)	114.3(4)
N(4)-Zn(1)-N(1)	120.0(2)	C(28)-O(4)-Zn(1)	126.0(4)
N(4)-Zn(1)-N(2)	156.3(2)	C(5)-N(1)-Zn(1)	128.6(6)
N(1)-Zn(1)-N(2)	79.8(2)	C(1)-N(1)-Zn(1)	113.9(5)
N(4)-Zn(1)-N(3)	79.72(19)	C(6)-N(2)-Zn(1)	114.1(5)
N(1)-Zn(1)-N(3)	101.3(2)	C(8)-N(2)-Zn(1)	122.8(5)
N(2)-Zn(1)-N(3)	110.7(2)	C(19)-N(3)-Zn(1)	128.5(5)
N(4)-Zn(1)-O(4)	72.55(17)	C(15)-N(3)-Zn(1)	112.5(4)
N(1)-Zn(1)-O(4)	90.7(2)	C(20)-N(4)-Zn(1)	114.2(4)
N(2)-Zn(1)-O(4)	95.98(19)	C(22)-N(4)-Zn(1)	122.5(4)
N(3)-Zn(1)-O(4)	152.17(19)		
Zn4			
Parameter		Parameter	
Zn(1)-N(1)	2.065(6)	Zn(2)-N(2)	2.073(6)
Zn(1)-N(3)	2.078(6)	Zn(2)-N(4)	2.071(6)

Zn(1)-Cl(1)	2.218(2)	Zn(2)-Cl(3)	2.185(2)
Zn(1)-Cl(2)	2.196(2)	Zn(2)-Cl(4)	2.203(2)
N(3)-C(6)	1.262(9)	N(4)-C(13)	1.259(10)
N(1)-Zn(1)-N(3)	80.3(3)	N(2)-Zn(2)-N(4)	79.9(3)
N(1)-Zn(1)-Cl(1)	106.95(17)	N(2)-Zn(2)-Cl(3)	114.59(18)
N(3)-Zn(1)-Cl(1)	113.3(2)	N(4)-Zn(2)-Cl(3)	120.42(18)
N(1)-Zn(1)-Cl(2)	115.90(19)	N(2)-Zn(2)-Cl(4)	112.73(16)
N(3)-Zn(1)-Cl(2)	114.15(19)	N(4)-Zn(2)-Cl(4)	105.21(19)
Cl(2)-Zn(1)-Cl(1)	119.61(9)	Cl(3)-Zn(2)-Cl(4)	117.94(9)
C(5)-N(1)-Zn(1)	129.2(6)	C(12)-N(2)-Zn(2)	129.4(5)
C(1)-N(1)-Zn(1)	111.9(5)	C(8)-N(2)-Zn(2)	111.9(5)
C(6)-N(3)-Zn(1)	112.0(6)	C(13)-N(4)-Zn(2)	113.1(6)
C(21)-N(3)-Zn(1)	129.2(6)	C(22)-N(4)-Zn(2)	127.2(6)

Zn5

Parameter		Parameter	
Zn(1)-N(1)	2.070(3)	N(1)-Zn(1)-Cl(2)	112.38(9)
Zn(1)-N(2)	2.093(3)	N(2)-Zn(1)-Cl(2)	108.08(9)
Zn(1)-Cl(1)	2.1779(11)	Cl(1)-Zn(1)-Cl(2)	118.11(5)
Zn(1)-Cl(2)	2.2154(12)	C(5)-N(1)-Zn(1)	129.8(3)
N(2)-C(10)	1.268(5)	C(1)-N(1)-Zn(1)	111.5(3)
N(1)-Zn(1)-N(2)	80.71(13)	C(10)-N(2)-Zn(1)	110.9(3)
N(1)-Zn(1)-Cl(1)	116.68(9)	C(11)-N(2)-Zn(1)	126.0(3)
N(2)-Zn(1)-Cl(1)	114.81(9)		

Table S3. Analytical and physical data of the ligands **L^1**–**L^5** and complexes **Zn1**–**Zn5**.

			Found (Calcd.) (%)			
Complex	Color	Yield (%)	C	H	N	M.p. (℃)
L^1	Yellow	67	63.38 (63.43)	3.41 (3.99)	18.45 (18.49)	130.2–131.5
Zn1	Yellow	58	39.72 (39.65)	2.61 (2.50)	11.58 (11.56)	—
L^2	Yellow	90	79.55 (79.56)	6.17 (6.16)	14.28 (14.27)	67.5–68.7
Zn2	Colorless	65	47.01 (46.96)	3.57 (3.64)	8.40 (8.42)	—
L^3	Yellow	89	69.17 (69.41)	5.99 (5.82)	11.38 (11.56)	55.0–56.3
Zn3	Yellow	72	44.88 (44.91)	3.81 (3.77)	7.43 (7.48)	—
L^4	Cream	80	70.68 (70.57)	5.94 (5.92)	14.88 (14.96)	74.6–75.6
Zn4	Colorless	67	40.85 (40.84)	3.47 (3.43)	8.59 (8.66)	—
L^5	Yellow	74	85.75 (85.69)	5.28 (5.23)	9.05 (9.08)	125.1–126.8
Zn5	Yellow	59	59.37 (59.43)	3.66 (3.63)	6.25 (6.30)	—

Table S4. The emission energy data of the ligands **L[1]**–**L[5]** and complexes **Zn1**–**Zn5** in acetonitrile solution and the solid state at room temperature.

Complex	in acetonitrile solution	in the solid state	$\Delta E_{(aq\text{-}solid)}$ [a] (eV)
	*E*max em (eV)	*E*max em (eV)	
L[1]	3.18	2.78	0.40
Zn1	2.88	2.69	0.19
L[2]	3.02	2.62	0.40
Zn2	2.99	2.57	0.42
L[3]	2.95	2.38	0.57
Zn3	2.41	2.33	0.08
L[4]	2.88	2.63	0.25
Zn4	2.70	2.41	0.29
L[5]	2.67	2.34	0.33
Zn5	2.21	2.09	0.12

[a] $\Delta E_{(aq\text{-}solid)}$ represents the maximum emission energy difference between the compound in acetonitrile solution and the solid state.

Table S5. The luminescence lifetimes of the ligands **L[1]**–**L[5]** and complexes **Zn1**–**Zn5** in acetonitrile solution and the solid state at room temperature.

Complex	τ_1 (μs)	A_1 (%)	τ_2 (μs)	A_2 (%)	τ^a (μs)	Conditions
L[1]	0.84	81.22	6.83	18.78	4.75	CH_3CN
	1.28	51.55	8.81	48.45	7.80	solid
Zn1	0.90	60.97	8.68	39.03	7.60	CH_3CN
	1.22	54.54	8.99	45.46	7.90	solid
L[2]	0.92	75.68	7.39	24.32	5.58	CH_3CN
	1.29	54.70	8.84	45.30	7.71	solid
Zn2	1.10	48.21	8.75	51.79	7.95	CH_3CN
	0.95	59.21	10.52	40.79	9.41	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	1.09	63.22	10.19	36.78	8.78	CH_3CN
	1.45	56.51	16.12	43.49	14.58	solid
L[4]	0.99	48.32	8.21	51.68	7.48	CH_3CN
	1.05	61.08	9.22	38.92	7.98	solid
Zn4	1.06	53.16	8.96	46.84	8.02	CH_3CN
	1.24	48.48	11.00	51.52	10.06	solid
L[5]	0.87	61.32	7.71	38.68	6.67	CH_3CN
	0.83	49.92	8.71	50.08	8.03	solid
Zn5	0.95	49.68	9.26	50.32	8.50	CH_3CN
	0.86	56.78	10.31	43.22	9.38	solid

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