Supporting Information

Luminescent Properties of Zn(II) Supramolecular Framework: Easily Tunable Optical Properties by Variation of the Alkyl Substitution of (*E*)-*N*-(Pyridine-2-ylethylidyne)arylamine Ligands

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Experimental Section

Lifetime Calculations. Lifetime studies were performed using photon-counting system with a microsecond pulse lamp as the excitation source. The emission decays were analyzed by the sum of exponential functions. The decay curve is well fitted into a double exponential function:[1] I (t) = A_1 exp ($-t/\tau_1$) + A_2 exp ($-t/\tau_2$), where I is the luminescence intensity, and τ_1 and τ_2 are the lifetimes for the exponential components. The average lifetime was calculated according to the following equation: $\frac{\tau_1^2 A_1\% + \tau_2^2 A_2\%}{\tau_1 A_1\% + \tau_2 A_2\%}$ (1).

Quantum Yield Measurements. Reference on quantum yield measurements: Lakowicz, J. R. *Principles of Fluorescence Spectroscopy,* 2nd Ed., **1999**, Kluwer Academic/Plenum Publishers, New York. Quinine sulfate in 0.1 M H_2SO_4 (quantum yield 0.546 at 350 nm) was chosen as a standard.[2–4] Absolute values are calculated using the standard reference sample that has a fixed and known fluorescence quantum yield value, according to the following equation: $Q = Q_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n^2}{n_R^2}$ (2). In equation (2), Q is the quantum yield, I is the measured integrated emission intensity, n is the refractive index, and OD is the optical density. The subscript R refers to the reference fluorophore of known quantum yield. In order to minimize re-absorption effects absorbencies in the 10 mm fluorescence cuvette were kept under 0.05 at the excitation wavelength (350 nm).

Synthesis of Ligand. The Schiff base ligands **L[1]–L[5]** were synthesized by dissolving 2-acetylpyridine in anhydrous methanol (10 mL) and 1 molar equivalence of the respective aniline derivatives (aniline, 2-methylaniline, 2,6-dimethylaniline, 2,4,6-trimethylaniline, and 2-methoxyaniline) in anhydrous methanol (10 mL) and mixing the two. The resultant solutions were set at reflux for *ca*. 8−12 h and subsequently concentrated under reduced pressure to obtain brown oil-like crude products.

N-((pyridin-2-yl)ethylidene)aniline (***L[1]***). 2-acetylpyridine (1.58 mL, 14.13 mmol) and aniline (1.29 mL, 14.15 mmol) gave 2.53 g of product (yield: 91%). Anal. Calcd (%) for $C_{13}H_{12}N_2$ (M = 196.25 g mol^{-1}): C, 79.56; H, 6.16; N, 14.27. Found: C, 79.61; H, 6.15; N, 14.23. FT-IR (KBr, cm^{-1}): 3434(w), 3070(w), 2962(m), 2871(w), 1625(s), 1586(m), 1567(w), 1460(s), 1438(s), 1385(m), 1297(w), 1282(m), 1265(m), 1238(m), 1146(w), 1117(w), 1101(w), 1057(w), 1044(m), 995(w), 956(w), 885(w), 824(w),

780(m), 745(m), 590(w), 533(w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, 1H, Py-H_6), 8.09 (d, 1H, Py-H_3), 7.86 (m, 1H, Py-H_4), 7.50 (m, 1H, Py-H_5), 6.84-7.19 (m, 5H, Ph-$H_{2,3,4,5,6}$), 2.77 (s, 3H, -CH_3) ppm.

(E)-2-Methyl-N-((pyridin-2-yl)ethylidene)aniline (***L²***). 2-acetylpyridine (1.27 mL, 11.33 mmol) and 2-methylaniline (1.21 mL, 11.31 mmol) gave 2.11 g of product (yield: 89%). Anal. Calcd (%) for $C_{14}H_{14}N_2$ (M = 210.28 g mol^{-1}): C, 79.97; H, 6.71; N, 13.32. Found: C, 80.03; H, 6.74; N, 13.29. FT-IR (KBr, cm^{-1}): 3433(w), 3056(w), 2918(w), 2860(w), 1643(s), 1584(m), 1568(w), 1499(m), 1468(m), 1437(m), 1358(s), 1299(m), 1282(s), 1239(m), 1222(w), 1190(w), 1148(w), 1102(m), 1043(m), 995(w), 955(w), 927(w), 837(w), 781(s), 743(s), 716(w), 623(w), 591(m), 537(w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, 1H, Py-H_6), 8.08 (d, 1H, Py-H_3), 7.84 (m, 1H, Py-H_4), 7.48 (m, 1H, Py-H_5), 6.68-7.08 (m, 4H, Ph-$H_{3,4,5,6}$), 2.77 (s, 3H, -CH_3), 2.19 (s, 3H, Ph-CH_3) ppm.

(E)-2,6-Dimethyl-N-((pyridin-2-yl)ethylidene)aniline (***L³***). 2-acetylpyridine (1.09 mL, 9.71 mmol) and 2,6-dimethylaniline (1.20 mL, 9.73 mmol) gave 1.76 g of product (yield: 81%). Anal. Calcd (%) for $C_{15}H_{16}N_2$ (M = 224.31 g mol^{-1}): C, 80.32; H, 7.19; N, 12.49. Found: C, 80.27; H, 7.18; N, 12.52. FT-IR (KBr, cm^{-1}): 3436(w), 3053(w), 2919(w), 2855(w), 1650(s), 1584(w), 1569(w), 1478(m), 1437(m), 1357(m), 1297(w), 1282(m), 1239(m), 1148(w), 1100(m), 1044(w), 995(w), 954(w), 897(w), 780(m), 760(m), 738(w), 683(w), 623(w), 590(m), 544(w), 491(w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, 1H, Py-H_6), 8.06 (d, 1H, Py-H_3), 7.85 (m, 1H, Py-H_4), 7.49 (m, 1H, Py-H_5), 6.67-6.98 (m, 3H, Ph-$H_{3,4,5}$), 2.77 (s, 3H, -CH_3), 2.21 (s, 6H, Ph-CH_3) ppm.

(E)-2,4,6-Trimethyl-N-((pyridin-2-yl)ethylidene)aniline (***L⁴***). 2-acetylpyridine (1.43 mL, 12.73 mmol) and 2,4,6-trimethylaniline (1.78 mL, 12.71 mmol) gave 2.80 g of product (yield: 92%). Anal. Calcd (%) for $C_{16}H_{18}N_2$ (M = 238.33 g mol^{-1}): C, 80.63; H, 7.61; N, 11.75. Found: C, 80.68; H, 7.67; N, 11.70. FT-IR (KBr, cm^{-1}): 3436(w), 3053(w), 2922(w), 2861(w), 1657(s), 1608(w), 1584(w), 1568(w), 1492(s), 1467(w), 1437(m), 1378(w), 1357(s), 1297(m), 1282(m), 1239(m), 1215(w), 1157(w), 1101(m), 1043(w), 1012(w), 995(w), 954(w), 856(m), 780(s), 742(w), 622(w), 590(m), 561(w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, 1H, Py-H_6), 8.08 (d, 1H, Py-H_3), 7.85 (m, 1H, Py-H_4), 7.49 (m, 1H, Py-H_5), 6.80 (s, 2H, Ph-$H_{3,5}$), 2.77 (s, 3H, -CH_3), 2.21 (t, 9H, Ph-

CH_3) ppm.

(E)-2-Methoxy-N-((pyridin-2-yl)ethylidene)aniline (***L*^{5}**). 2-acetylpyridine (2.0 mL, 17.83 mmol) and 2-methoxyaniline (1.85 mL, 16.49 mmol) gave 3.10 g of product (yield: 83%). Anal. Calcd (%) for $C_{14}H_{14}N_2O$ (M = 226.28 g mol^{-1}): C, 74.31; H, 6.24; N, 12.38. Found: C, 74.33; H, 6.25; N, 12.35. FT-IR (KBr, cm^{-1}): 3420(w), 3057(w), 2949(w), 2836(w), 1627(m), 1584(m), 1568(w), 1506(s), 1465(m), 1437(w), 1419(w), 1357(m), 1297(w), 1282(s), 1238(m), 1225(s), 1181(w), 1141(w), 1101(w), 1073(w), 1045(m), 1025(m), 995(w), 954(w), 910(w), 840(w), 781(m), 742(s), 622(w), 590(m), 453(w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, 1H, Py-H_6), 8.08 (d, 1H, Py-H_3), 7.85 (t, 1H, Py-H_4), 7.49 (t, 1H, Py-H_5), 6.80-6.83 (m, 4H, Ph-$H_{3,4,5,6}$), 3.87 (s, 3H, Ph-OCH_3), 2.76 (s, 3H, -CH_3) ppm.

References

(1) Y. W. Dong, R. Q. Fan, P. Wang, L. G. Wei, X. M. Wang, H. J. Zhang, S. Gao, Y. L. Yang and Y. L. Wang, *Dalton Trans*., 2015, **44**, 5306–5322.

(2) R. Z. Lakowicz, *Principles of fluorescence spectroscopy* (2nd Ed); Klumer Academic/Plenum Publisher: New York, 1999.

(3) H. Liu, T. Ye and C. Mao, *Angew. Chem., Int. Ed.,* 2007, **46**, 6473–6475.

(4) S. Chen, Y. K. Wu, Y. Zhao and D. N. Fang, *RSC Adv.,* 2015, **5**, 72009–72018.

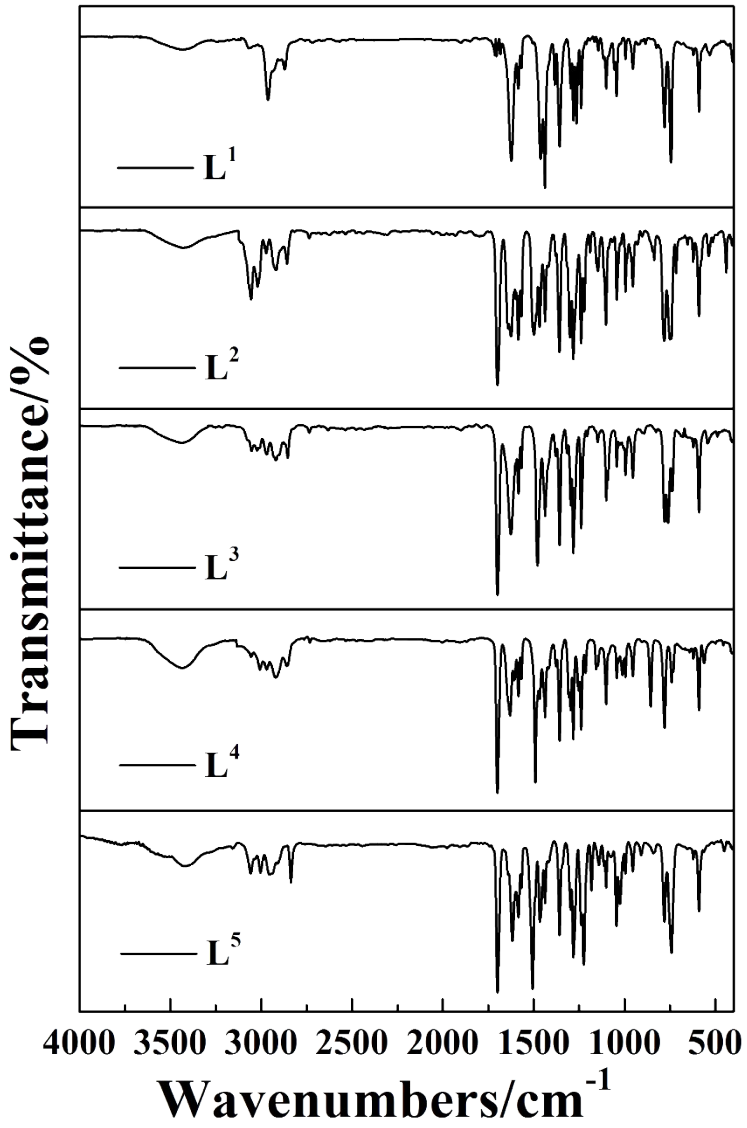

Figure S1. IR spectra of ligands $\mathbf{L^1}$–$\mathbf{L^5}$ in KBr disks.

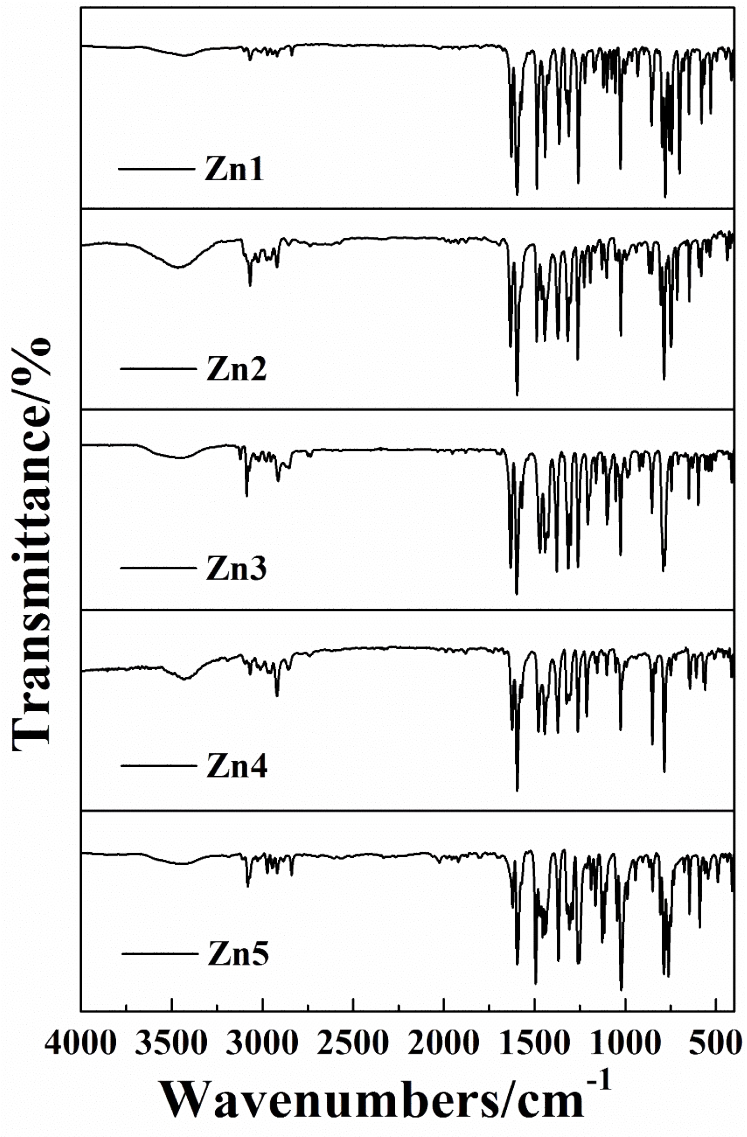

Figure S2. IR spectra of complexes **Zn1**–**Zn5** in KBr disks.

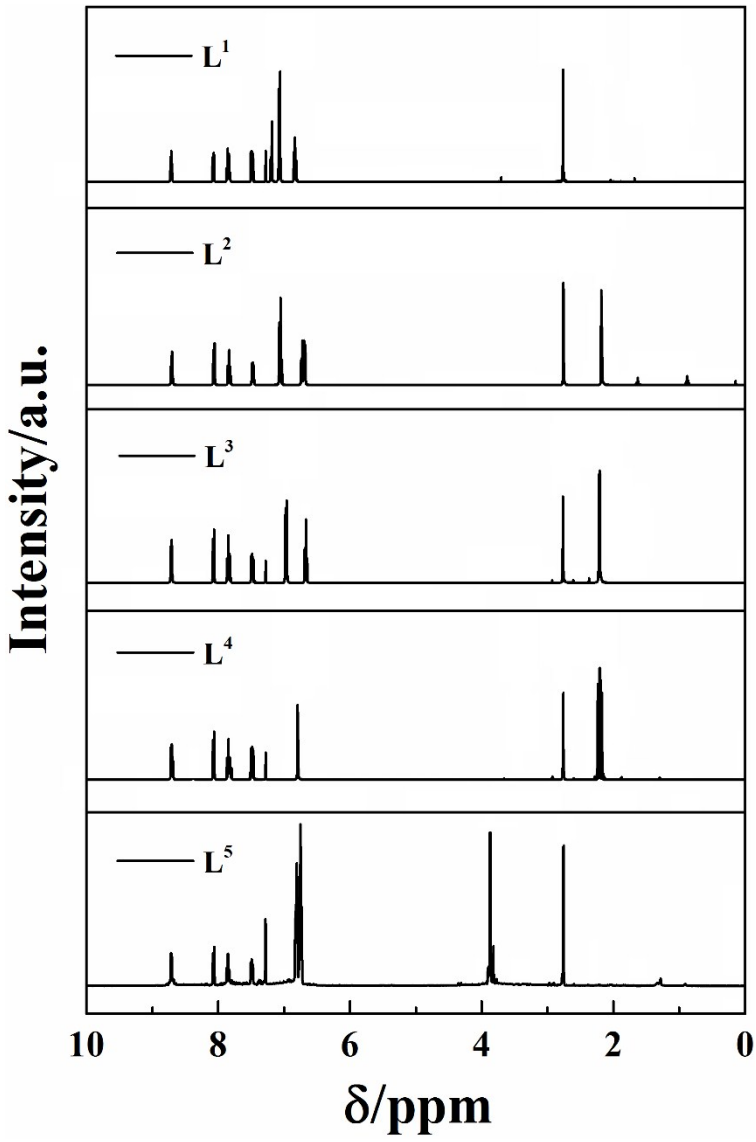

Figure S3. ^{1}H NMR spectra of ligands **L^{1}–L^{5}** in $CDCl_3$.

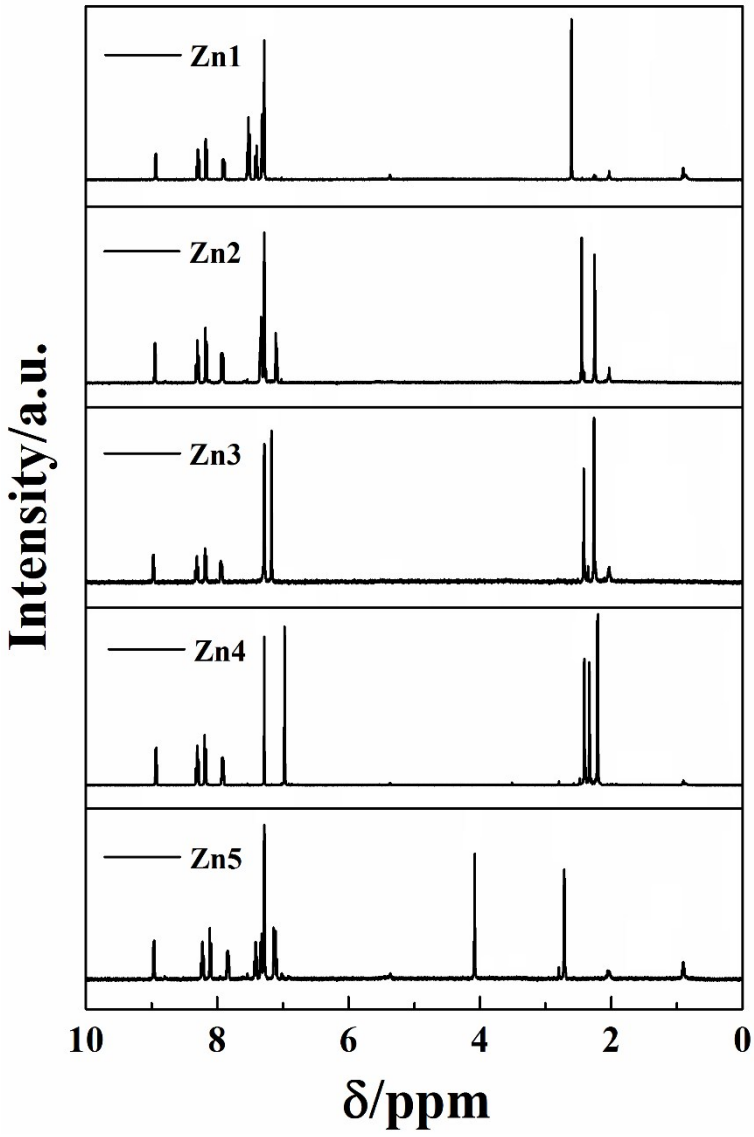

Figure S4. ^{1}H NMR spectra of complexes **Zn1**–**Zn5** in $CDCl_3$.

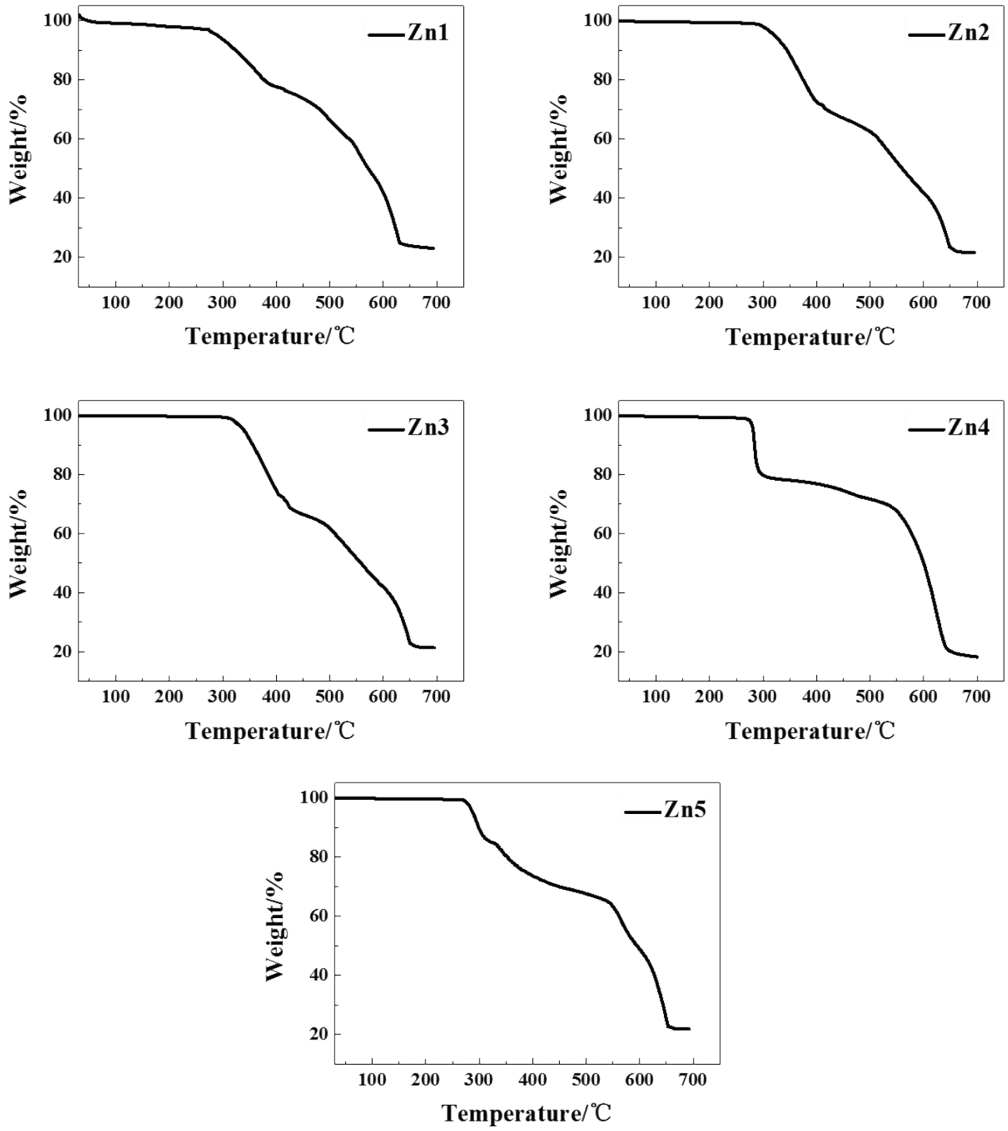

Figure S5. Thermal gravimetric curves of complexes **Zn1**–**Zn5**.

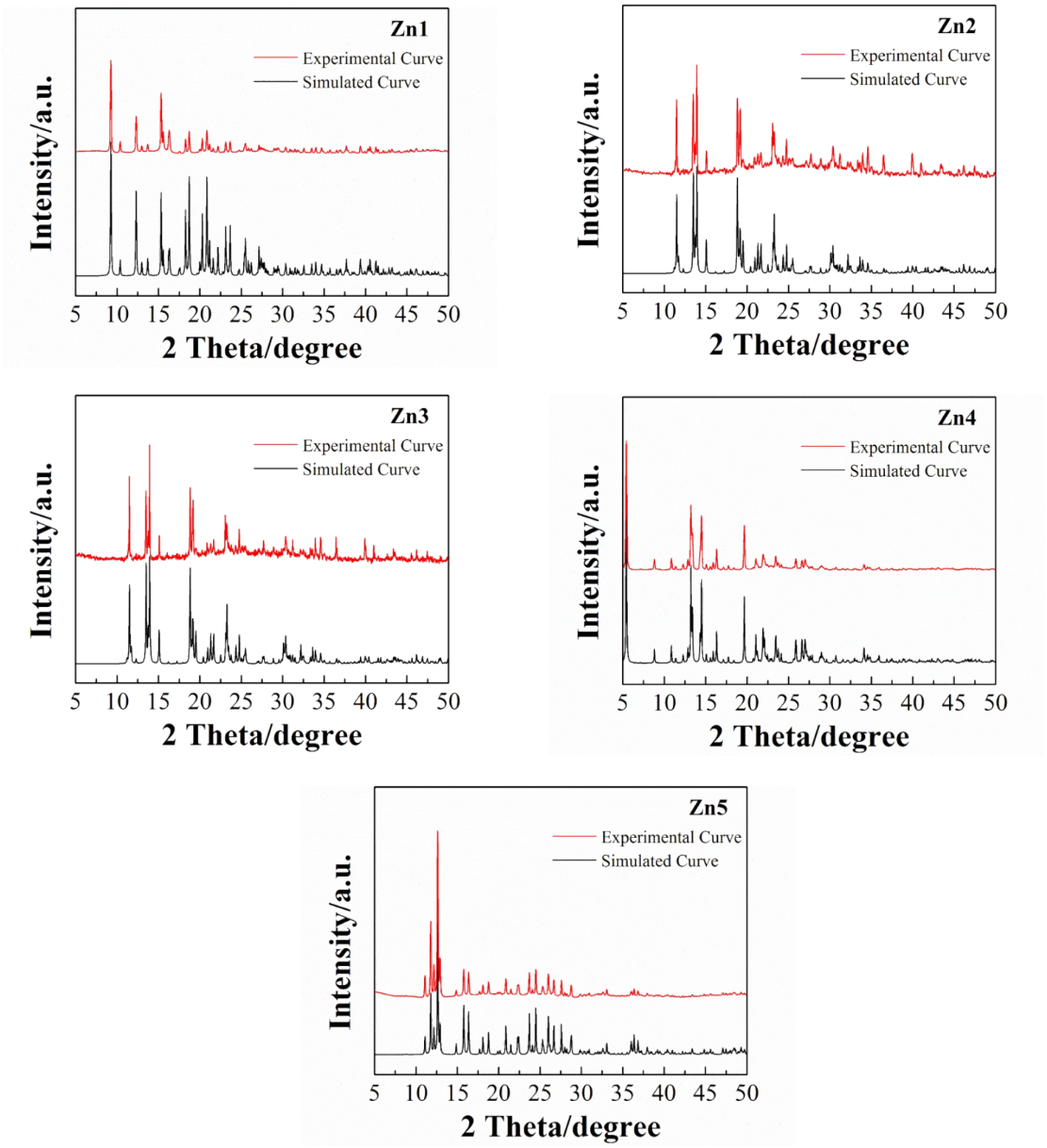

Figure S6. Experimental (top) and simulated (bottom) PXRD patterns of complexes **Zn1**–**Zn5**.

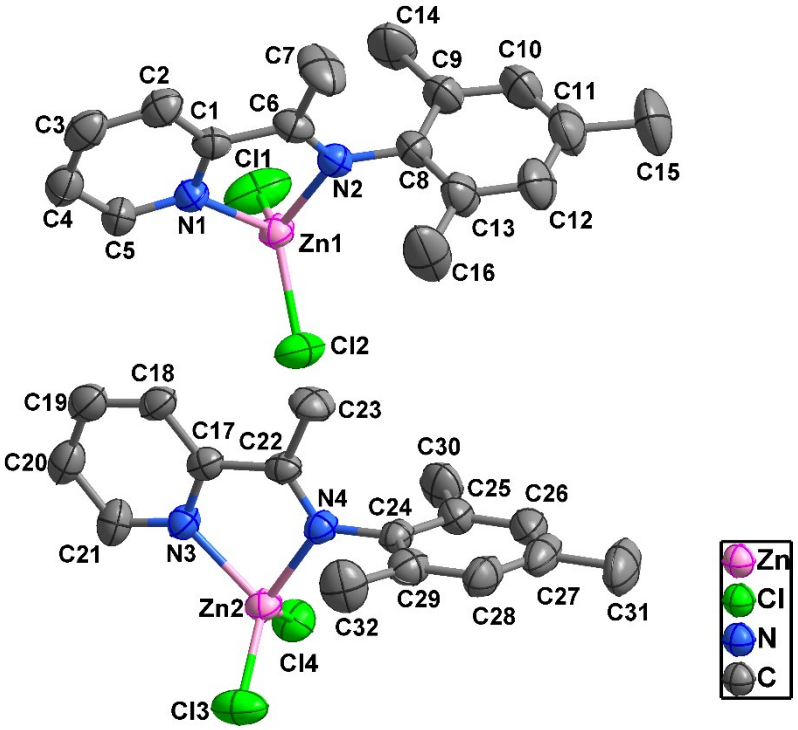

Figure S7. Crystal structure of **Zn4**. Thermal ellipsoid is drawn at 50% probability. H atoms have been omitted for clarity.

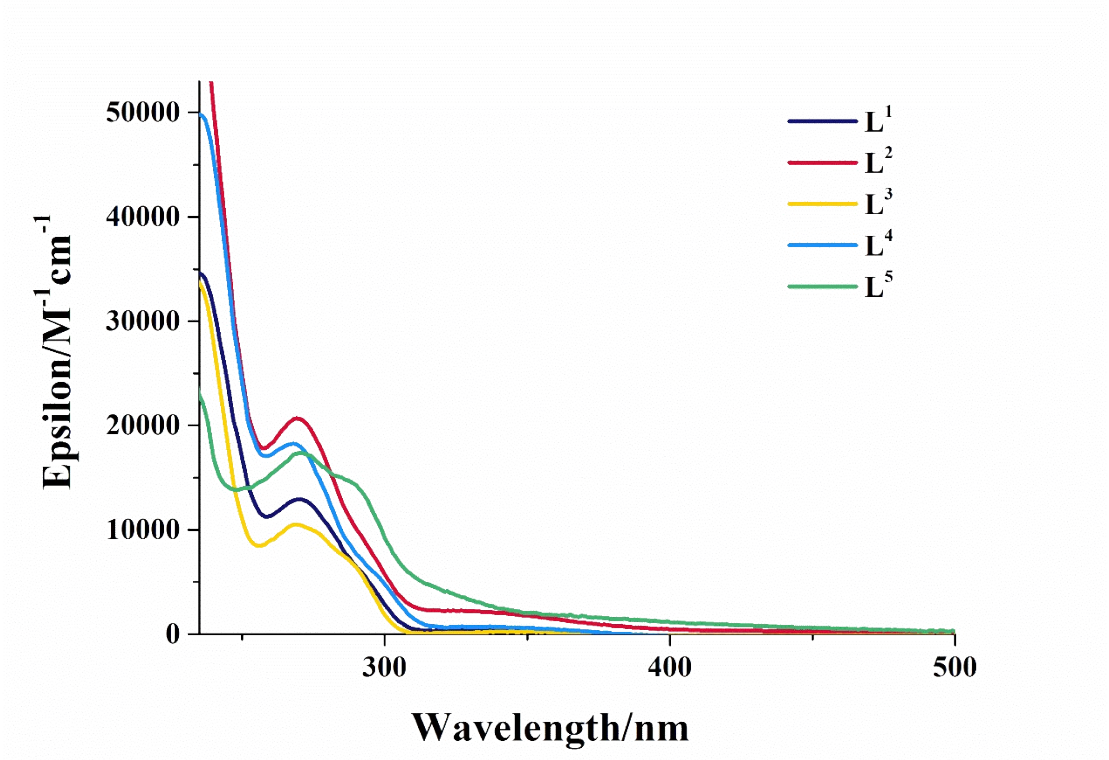

Figure S8. UV−vis absorption spectra of $\mathbf{L^1}$–$\mathbf{L^5}$ in CH_3CN at room temperature.

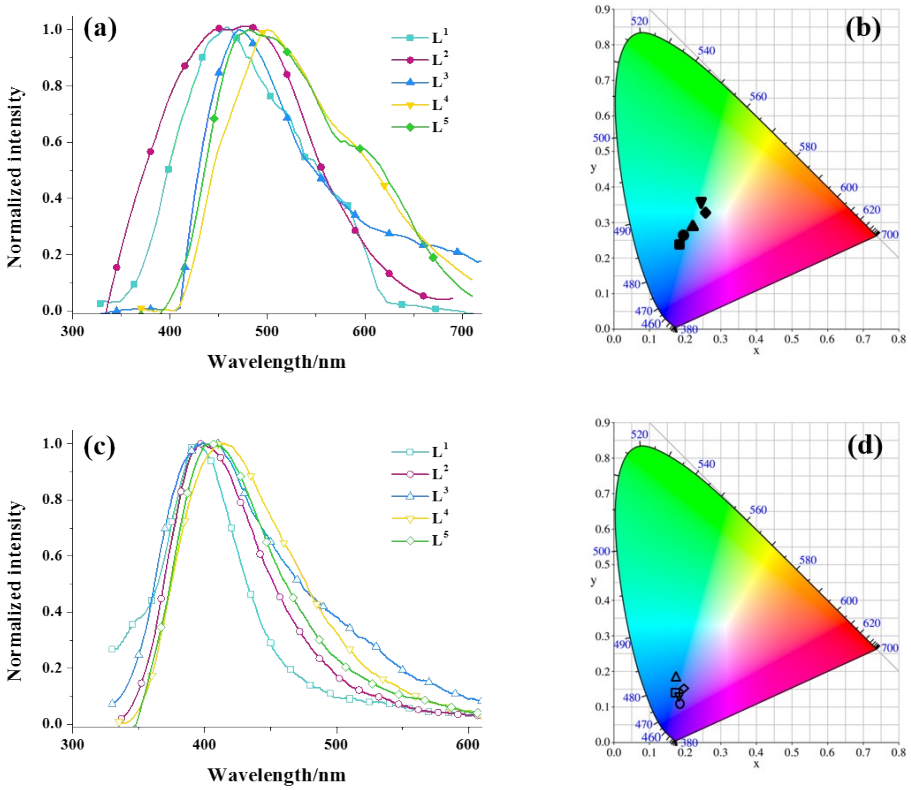

Figure S9. (a) Emission spectra of L^1–L^5 in the solid state and (b) CIE chromaticity diagram (1931 CIE standard). (c) Emission spectra of L^1–L^5 in acetonitrile solution and (d) CIE chromaticity diagram.

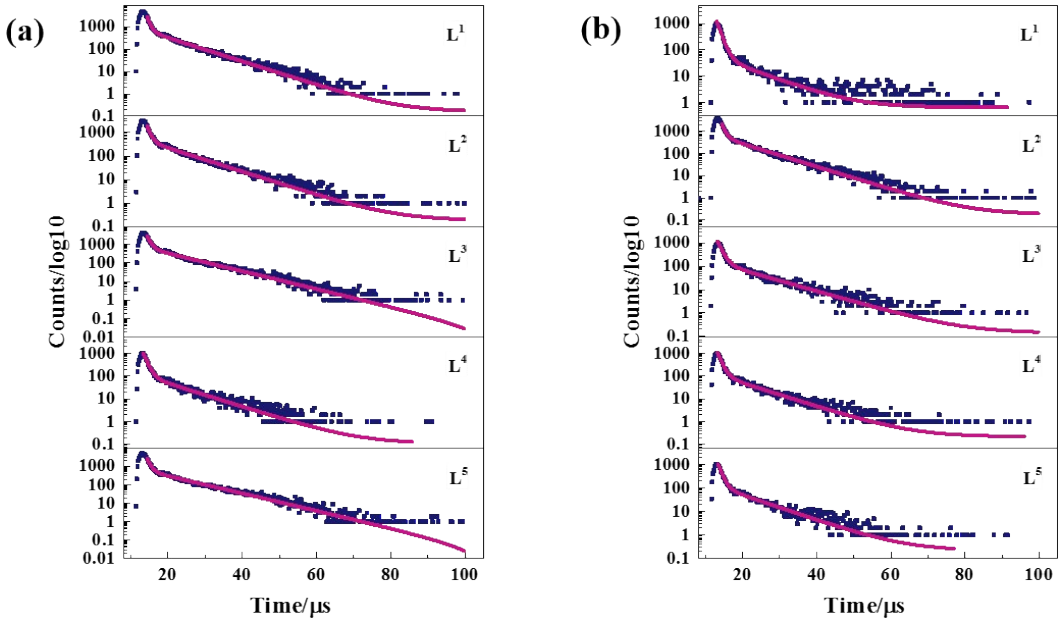

Figure S10. Luminescence decay profiles of the ligands L^1–L^5 in (a) the solid state and (b) acetonitrile solution.

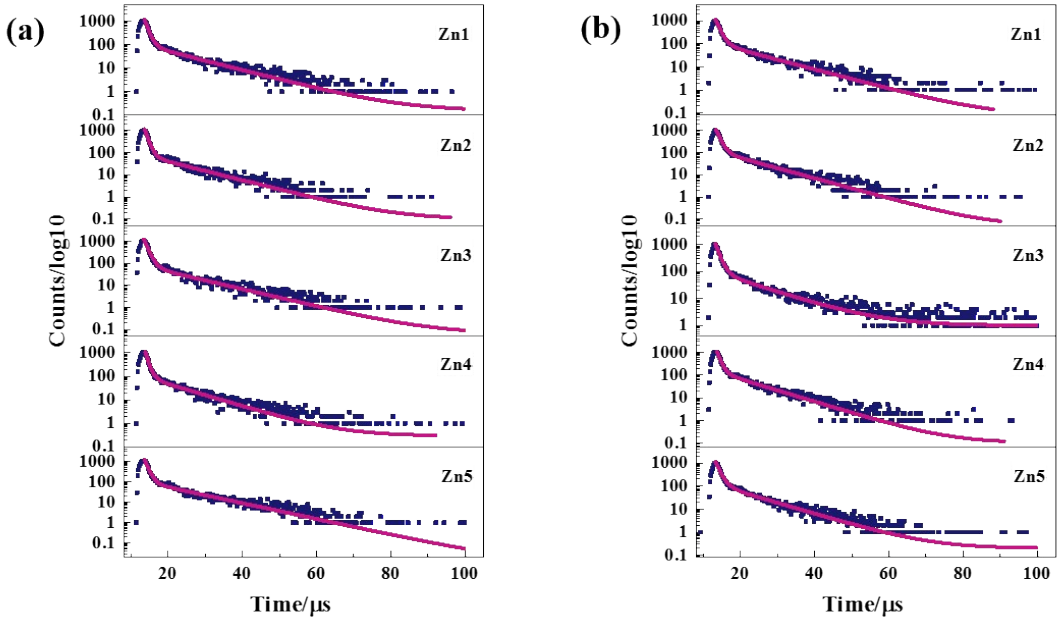

Figure S11. Luminescence decay profiles of the complexes **Zn1**–**Zn5** in (a) the solid state and (b) acetonitrile solution.

Table S1. Selected bond distances (Å) and angles (°) for **Zn1**, **Zn3** and **Zn5**.

Parameter	**Zn1**	**Zn3**	**Zn5**
Zn(1)-N(1)	2.051(3)	2.066(2)	2.087(2)
Zn(1)-N(2)	2.049(2)	2.0691(18)	2.083(2)
Zn(1)-Cl(1)	2.1955(10)	2.1979(8)	2.2233(8)
Zn(1)-Cl(2)	2.1915(9)	2.1969(9)	2.2233(10)
N(2)-C(6)	1.275(4)	1.278(3)	1.287(3)
N(1)-Zn(1)-N(2)	79.78(11)	79.73(8)	78.08(8)
N(1)-Zn(1)-Cl(1)	116.19(8)	114.58(6)	104.50(7)
N(2)-Zn(1)-Cl(1)	112.19(8)	111.04(6)	133.23(6)
N(1)-Zn(1)-Cl(2)	110.02(9)	109.19(7)	112.97(6)
N(2)-Zn(1)-Cl(2)	118.26(8)	118.90(6)	105.61(6)
Cl(1)-Zn(1)-Cl(2)	115.53(4)	117.55(4)	115.21(3)
C(5)-N(1)-Zn(1)	127.9(3)	127.87(17)	127.0(2)
C(1)-N(1)-Zn(1)	113.1(2)	112.92(15)	114.06(16)
C(6)-N(2)-Zn(1)	116.2(2)	114.86(16)	116.14(16)
C(8)-N(2)-Zn(1)	121.2(2)	123.22(14)	120.40(15)

Table S2. Selected bond distances (Å) and angles (°) for **Zn2** and **Zn4**.

Parameter	**Zn2**	Parameter	**Zn4**
Zn(1)-N(1)	2.073(3)	Zn(1)-N(1)	2.061(3)
Zn(1)-N(2)	2.055(3)	Zn(1)-N(2)	2.071(3)
Zn(1)-Cl(1)	2.2105(16)	Zn(1)-Cl(1)	2.2020(14)
Zn(1)-Cl(2)	2.1949(15)	Zn(1)-Cl(2)	2.1915(12)
N(2)-C(6)	1.277(4)	N(2)-C(6)	1.285(5)
Zn(2)-N(3)	2.068(3)	Zn(2)-N(3)	2.063(3)
Zn(2)-N(4)	2.055(3)	Zn(2)-N(4)	2.067(3)
Zn(2)-Cl(3)	2.1971(17)	Zn(2)-Cl(3)	2.2110(13)
Zn(2)-Cl(4)	2.1996(16)	Zn(2)-Cl(4)	2.1994(11)
N(4)-C(20)	1.284(4)	N(4)-C(22)	1.286(4)
N(1)-Zn(1)-N(2)	79.32(12)	N(1)-Zn(1)-N(2)	79.69(11)
N(1)-Zn(1)-Cl(1)	112.45(9)	N(1)-Zn(1)-Cl(1)	110.07(9)
N(2)-Zn(1)-Cl(1)	112.65(10)	N(2)-Zn(1)-Cl(1)	116.68(9)
N(1)-Zn(1)-Cl(2)	114.33(9)	N(1)-Zn(1)-Cl(2)	112.50(9)
N(2)-Zn(1)-Cl(2)	118.15(9)	N(2)-Zn(1)-Cl(2)	116.25(9)
Cl(1)-Zn(1)-Cl(2)	115.01(6)	Cl(1)-Zn(1)-Cl(2)	115.92(5)
C(5)-N(1)-Zn(1)	113.4(2)	C(5)-N(1)-Zn(1)	127.1(2)
C(1)-N(1)-Zn(1)	127.7(3)	C(1)-N(1)-Zn(1)	113.9(2)
C(6)-N(2)-Zn(1)	115.6(2)	C(6)-N(2)-Zn(1)	114.1(2)
C(8A)-N(2)-Zn(1)	124.2(3)	C(8)-N(2)-Zn(1)	124.9(2)
C(8B)-N(2)-Zn(1)	121.2(7)		
N(3)-Zn(2)-N(4)	79.61(12)	N(3)-Zn(2)-N(4)	79.77(10)
N(3)-Zn(2)-Cl(3)	113.08(9)	N(3)-Zn(2)-Cl(3)	115.39(9)
N(4)-Zn(2)-Cl(3)	117.95(10)	N(4)-Zn(2)-Cl(3)	111.57(8)
N(3)-Zn(2)-Cl(4)	112.85(9)	N(3)-Zn(2)-Cl(4)	108.61(8)
N(4)-Zn(2)-Cl(4)	111.57(9)	N(4)-Zn(2)-Cl(4)	119.01(8)
Cl(3)-Zn(2)-Cl(4)	116.39(5)	Cl(3)-Zn(2)-Cl(4)	116.92(5)

C(19)-N(3)-Zn(2)	113.1(2)	C(21)-N(3)-Zn(2)	127.0(2)
C(15)-N(3)-Zn(2)	128.1(2)	C(17)-N(3)-Zn(2)	113.7(2)
C(20)-N(4)-Zn(2)	115.7(2)	C(22)-N(4)-Zn(2)	114.5(2)
C(22A)-N(4)-Zn(2)	123.0(4)	C(24)-N(4)-Zn(2)	124.85(19)
C(22B)-N(4)-Zn(2)	122.8(11)		

Table S3. Summary of IR and ^{1}H NMR data for complexes **Zn1**–**Zn5**.

Complex	IR data (ν/cm^{-1})	^{1}H NMR data (δ/ppm)
Zn1	3429(w), 3069(w), 2943(w), 2838(w), 1623(m), 1596(s), 1573(s), 1486(s), 1442(m), 1423(w), 1364(m), 1322(w), 1312(m), 1258(s), 1222(w), 1173(w), 1164(w), 1121(w), 1100(w), 1076(w), 1055(w), 1026(s), 1001(w), 964(w), 932(w), 856(m), 797(m), 780(s), 757(s), 744(s), 702(s), 678(w), 649(m), 580(m), 565(w), 530(m), 496(w), 446(w)	8.94 (d, 1H, Py-H_6), 8.30 (d, 1H, Py-H_3), 8.18 (m, 1H, Py-H_4), 7.91 (m, 1H, Py-H_5), 7.30-7.53 (m, 5H, Ph-$H_{2,3,4,5,6}$), 2.60 (s, 3H, -CH_3)
Zn2	3449(w), 3067(w), 2955(w), 2854(w), 1632(m), 1596(s), 1570(m), 1488(m), 1459(w), 1443(m), 1370(m), 1317(m), 1304(w), 1262(m), 1226(w), 1193(w), 1167(w), 1129(w), 1101(w), 1053(w), 1024(m), 994(w), 939(w), 910(w), 868(w), 854(w), 804(m), 786(s), 749(s), 714(m), 647(m), 595(w), 581(w), 552(w), 533(w), 496(w), 438(w)	8.95 (d, 1H, Py-H_6), 8.30 (d, 1H, Py-H_3), 8.18 (m, 1H, Py-H_4), 7.92 (m, 1H, Py-H_5), 7.09-7.33 (m, 4H, Ph-$H_{3,4,5,6}$), 2.45 (s, 3H, -CH_3), 2.25 (s, 3H, Ph-CH_3)
Zn3	3442(w), 3073(w), 2912(w), 2852(w), 1631(m), 1598(s), 1569(w), 1470(m), 1441(m), 1425(w), 1425(w), 1377(s), 1314(s), 1300(m), 1260(s), 1207(m), 1162(w), 1123(w), 1100(m), 1053(w), 1025(m), 987(w), 922(w), 903(w), 854(m), 791(s), 782(s), 746(s), 708(w), 649(w), 628(w), 598(w), 558(w), 541(w), 525(w), 503(w), 439(w)	8.98 (d, 1H, Py-H_6), 8.31 (d, 1H, Py-H_3), 8.19 (m, 1H, Py-H_4), 7.94 (t, 1H, Py-H_5), 7.17 (s, 3H, Ph-$H_{3,4,5}$), 2.42 (s, 3H, -CH_3), 2.26 (s, 6H, Ph-CH_3)
Zn4	3428(w), 3067(w), 2920(w), 2857(w), 1623(m), 1595(s), 1570(w), 1478(m), 1443(m), 1371(m), 1323(w), 1308(w), 1260(m), 1213(m), 1166(w), 1155(w), 1119(w), 1101(w), 1053(w), 1025(s), 994(w), 939(w), 851(s), 833(w), 785(s), 749(w), 722(w), 642(w), 609(w), 569(w), 560(w), 510(w), 457(w), 433(w)	8.94 (d, 1H, Py-H_6), 8.31 (d, 1H, Py-H_3), 8.19 (m, 1H, Py-H_4), 7.92 (m, 1H, Py-H_5), 6.97 (s, 2H, Ph-$H_{3,5}$), 2.41 (s, 3H, -CH_3), 2.33 (s, 3H, Ph-CH_3), 2.21 (s, 3H, Ph-CH_3)
Zn5	3431(w), 3069(w), 2946(w), 2839(w), 1620(w), 1595(s), 1494(s), 1455(w), 1443(m), 1368(s), 1321(w), 1308(m), 1291(m), 1259(s), 1189(w), 1165(w), 1128(m), 1115(m), 1103(w), 1046(m), 1022(s), 988(w), 943(w), 904(w), 867(w), 850(w), 807(w), 787(s), 762(s), 733(w), 676(w), 646(m), 590(m), 561(w), 545(w), 488(w), 437(w)	8.97 (d, 1H, Py-H_6), 8.23 (d, 1H, Py-H_3), 8.11 (t, 1H, Py-H_4), 7.84 (t, 1H, Py-H_5), 7.09-7.42 (m, 4H, Ph-$H_{3,4,5,6}$), 4.08 (s, 3H, Ph-OCH_3), 2.72 (s, 3H, -CH_3)

Table S4. 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]	1.07	76.88	8.27	23.12	6.10	CH_3CN
	0.78	27.74	8.19	72.26	7.93	solid
Zn1	1.10	55.84	10.27	44.16	9.15	CH_3CN
	0.94	54.70	10.84	45.30	9.90	solid
L[2]	0.86	27.36	8.38	72.64	8.10	CH_3CN
	0.87	28.97	8.64	71.03	8.33	solid
Zn2	1.05	52.59	9.46	47.41	8.54	CH_3CN
	0.87	60.79	10.22	39.21	9.13	solid
L[3]	1.15	51.34	9.57	48.66	8.62	CH_3CN
	0.90	28.38	9.04	71.62	8.73	solid
Zn3	1.07	57.71	9.79	42.29	8.66	CH_3CN
	1.04	63.25	11.03	36.75	9.64	solid
L[4]	1.03	56.04	8.43	43.96	7.43	CH_3CN
	1.02	53.90	8.47	46.10	7.55	solid
Zn4	0.94	47.40	8.77	52.60	8.08	CH_3CN
	0.79	54.02	9.14	45.98	8.37	solid
L[5]	0.98	53.16	8.13	46.84	7.27	CH_3CN
	0.84	28.83	9.21	71.17	8.91	solid
Zn5	1.13	56.37	9.14	43.63	8.04	CH_3CN
	0.96	54.24	11.19	45.76	10.25	solid

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