

Supporting Information

ESIPT-AIE Active Schiff Base Based on 2-(2'-Hydroxyphenyl)benzothiazole Applied as Multi-functional Fluorescent Chemosensors

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Experimental Section

1. Materials and instrumentation

All solvents and reagents (analytical grade and spectroscopic grade) were used as received. Aqueous solutions of different metal ions were prepared with LiCl, NaCl, KNO₃, CaCl₂, MgCl₂·6H₂O, Al(ClO₄)₃·9H₂O, CrCl₃·6H₂O, Mn(ClO₄)₂·6H₂O, Co(ClO₄)₂·6H₂O, Ni(ClO₄)₂·6H₂O, FeCl₃, Cu(ClO₄)₂·6H₂O, Zn(ClO₄)₂·6H₂O, Cd(ClO₄)₂·6H₂O, Hg(ClO₄)₂·3H₂O and Pb(ClO₄)₂·3H₂O. C, H and N elemental analyses were collected with a Vario EL elemental analyser. Fourier transform infrared (FT-IR) spectra were measured on an Avatar 360 FT-IR spectrometer using KBr pellets in 4000-400 cm⁻¹. The UV-Vis absorption spectra and fluorescence spectra were measured by a UV-2450 spectrophotometer and a FS5 fluorescence spectrophotometer with a quartz cuvette (path length = 1 cm), respectively. ¹H NMR spectra were recorded on a Bruker Avance III 600 MHz spectrometer. DLS (dynamic light scattering) data were obtained on Brookhaven Zeta Plus Zeta Potential Analyzer. High-resolution ESI-MS spectra were collected on an AB SCIEX Triple TOF 5600+ mass spectrometer. Powder X-Ray diffraction (PXRD) patterns were performed on an X'Pert PRO MPD diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 25°C. Single crystal data were collected on a Bruker Smart APEXII CCD diffractometer with Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$) at 150 K. The crystal structures were solved by the direct method and refined using the Olex2 program. Hydrogen atoms were placed in calculated positions.

2. Synthesis of HL¹

3-(2-benzothiazolyl)-2-hydroxybenzaldehyde was synthesized according to the literature [1]. A mixture of compound 3-(2-benzothiazolyl)-2-hydroxybenzaldehyde (0.0255 g, 0.1 mmol) and phenylmethanamine (0.0107 g, 0.1 mmol) in methanol (8 ml) was heated at 80 °C and refluxed for 6 hours, then cooled to room temperature. Orange-red needle-like crystals of HL¹ were obtained, the yield was 69.0%. Anal. Calcd: C, 73.23%; H, 4.68%; N, 8.13%; Found: C, 73.02%; H, 4.71%; N, 7.80%. IR (KBr pellet, cm⁻¹): 3417.86 m, 3061.03 w, 3024.38 w, 1627.92 s, 1614.42 s, 1498.69 s, 1454.33 s, 1440.83 m, 1423.47 m, 1373.32 w, 1321.24 m, 1274.95 w, 1215.15 w, 1176.58 w, 1037.70 m, 759.23 s, 696.30 s. ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 15.06 (s, 1H), 8.87 (s, 1H), 8.56 (d, J = 7.9 Hz, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.56-7.33 (m, 7H), 6.77 (t, J = 7.6 Hz, 1H), 4.96 (s, 2H).

3. Synthesis of HL²

3-(2-benzothiazolyl)-2-hydroxybenzaldehyde (0.0127 g, 0.05 mmol) and diphenylmethanamine (0.0092 g, 0.05 mmol) were mixed in 2 mL methanol in a 25 mL Teflon-lined autoclave, heated at 80 °C for one day and then cooled to room temperature. The yellow flake crystal was obtained after volatilization of the solution at room temperature, the yield was 61.4%. Anal. Calcd: C, 77.12%; H, 4.79%; N, 6.66%; Found: C, 76.78%; H, 4.68%; N, 6.38%. IR (KBr pellet, cm⁻¹): 3421.72 m, 3059.10 w, 3032.10 w, 1626.47 s, 1606.71 s, 1490.97 m, 1452.40 w, 1425.40 m, 1381.03 w, 1311.59 m, 1265.30 w, 1134.14 w, 1076.28 m, 1039.63 s, 746.45 m, 698.23 m. ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 16.05 (s, 1H), 8.94 (s, 1H), 8.56 (d, J = 7.4, 1H), 8.12 (d, J = 8.0, 1H), 8.03 (d, J = 8.1, 1H), 7.69 (d, J = 7.4, 1H), 7.58-7.29 (m, 12H), 7.00 (td, J = 7.7, 2.2, 1H), 6.13 (s, 1H).

4. Synthesis of HL³

3-(2-benzothiazolyl)-2-hydroxybenzaldehyde (0.0127 g, 0.05 mmol) and triphenylmethanamine (0.0130 g, 0.05 mmol) were mixed in 3 mL methanol in a 25 mL Teflon-lined autoclave, heated at 80 °C for one day and then cooled to room temperature. The orange-yellow flake crystal was obtained and the yield was 63.3%. Anal. Calcd: C, 79.81%; H, 4.87%; N, 5.64%; Found: C, 79.47%; H, 4.97%; N, 5.44%. IR (KBr pellet, cm⁻¹): 3419.79 m, 3062.52 w, 3024.64 w, 1622.13 s, 1600.92 s, 1488.42 s, 1455.38 m, 1444.68 s, 1429.25 m, 1313.52 m, 1296.16 m, 1256.66 w, 1233.89 w, 1031.92 m, 1010.70 m, 761.88 s, 698.55 s. ¹H NMR (400 MHz, Chloroform-*d*): δ (ppm) = 16.03 (s, 1H), 8.68 (s, 1H), 8.13 (d, J = 8.0 Hz, 1H), 8.08 (s, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.43-7.28 (m, 11H), 7.25-7.21 (m, 6H), 7.00 (t, J = 7.7 Hz, 1H).

5. Synthesis of ZnL¹₂

A mixture of compound Zn(ClO₄)₂·6H₂O (0.0093 g, 0.025 mmol), 3-(2-benzothiazolyl)-2-hydroxybenzaldehyde (0.0127 g, 0.05 mmol) and phenylmethanamine (0.0054 g, 0.05 mmol) in methanol (10 ml) was heated at 80 °C and refluxed for 6 hours, then cooled to room temperature, yellow-green powder precipitates. After filtering, the powder was recrystallized in MeOH/DMSO (V/V=2/1) mixed solvent to obtain light yellowish green block crystal, the yield was 52.9%. Anal. Calcd: C, 67.06%; H, 4.02%; N, 7.45%; Found: C, 65.97%; H, 4.136%; N, 7.01%. IR

(KBr pellet, cm^{-1}): 3423.65 m, 3064.89 w, 3030.17 w, 1620.57 s, 1550.77 s, 1477.47 w, 1454.33 w, 1433.11 m, 1400.32 w, 1309.67 m, 1222.87 m, 1047.35 m, 923.90 w, 752.42 m, 698.23 w.

6. Synthesis of ZnL_2

$\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0093 g, 0.025 mmol), 3-(2-benzothiazolyl)-2-hydroxybenzaldehyde (0.0127 g, 0.05 mmol) and diphenylmethanamine (0.0092 g, 0.05 mmol) were mixed in 3 mL acetonitrile in a 25 mL Teflon-lined autoclave, heated at 80 °C for two days and then cooled to room temperature. The yellow block crystal was obtained, the yield was 36.3%. Anal. Calcd: C, 71.71%; H, 4.23%; N, 6.19%; Found: C, 70.33 %; H, 4.21%; N, 6.13%. IR (KBr pellet, cm^{-1}): 3431.36 m, 3057.17 w, 3024.38 w, 1604.77 s, 1544.98 s, 1494.83 m, 1452.40 m, 1435.04 m, 1409.96 m, 1309.67 m, 1222.87 m, 1043.49 m, 871.82 w, 754.17 s, 696.30 m.

7. X-ray analysis

The single-crystal X-ray diffraction data of HL^1 , HL^2 , HL^3 , ZnL_1 and ZnL_2 crystals were collected on the Bruker APEX II CCD diffractometer with Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$). The crystal structures were solved and refined using the Olex2 program and all hydrogen atoms were added automatically. Crystal data and structure refinement parameters were summarized in Table S1 and Table S2. Selected bond distances (\AA) and angles (deg) for ZnL_1 and ZnL_2 were displayed in Table S3. The pictures were created with the Diamond program.

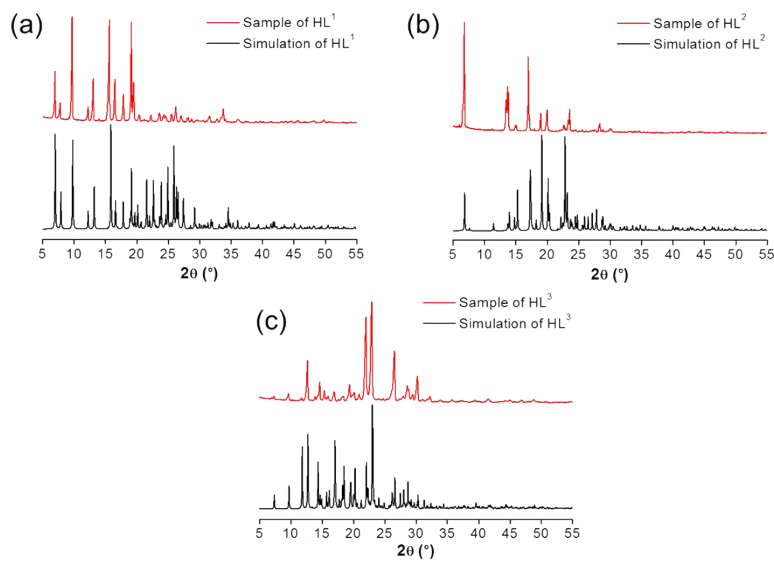


Figure S1 Powder diffraction patterns and theoretical simulations of (a) HL^1 / (b) HL^2 / (c) HL^3 samples.

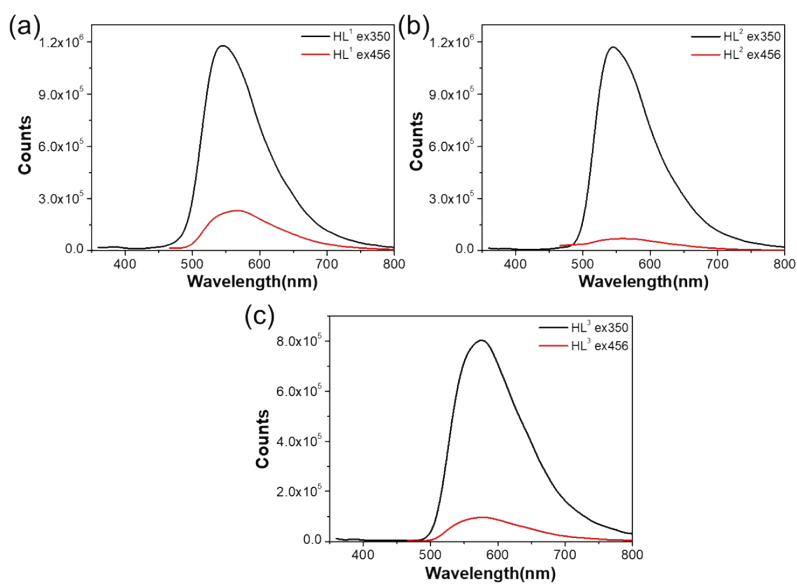


Figure S2 The fluorescence emission spectra of HL^1 , HL^2 and HL^3 in THF, $\lambda_{ex} = 350$ nm, 456 nm.

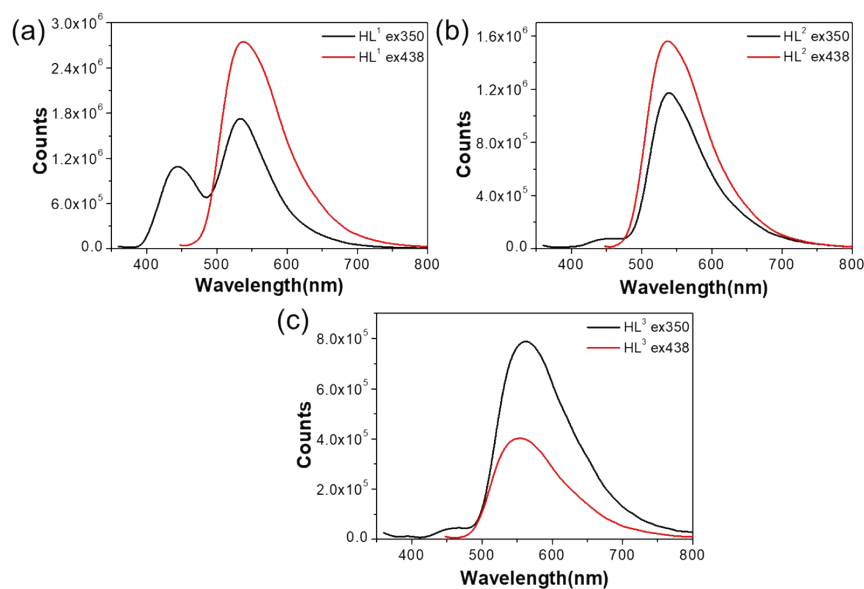


Figure S3 The fluorescence emission spectra of HL¹, HL² and HL³ in THF/HEPES (3:7, v/v, pH = 7.4), $\lambda_{\text{ex}} = 350 \text{ nm}, 438 \text{ nm}$.

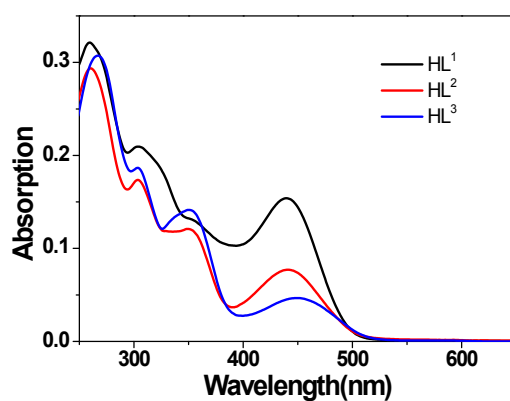


Figure S4 The absorption spectra of HL¹, HL² and HL³ in THF/HEPES (3:7, v/v, pH = 7.4).

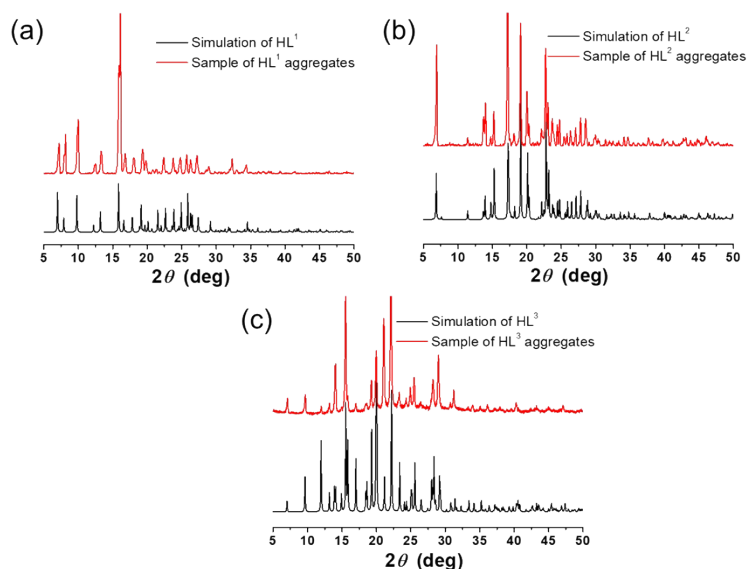


Figure S5 Powder diffraction patterns of (a) HL^1 / (b) HL^2 / (c) HL^3 aggregates samples.

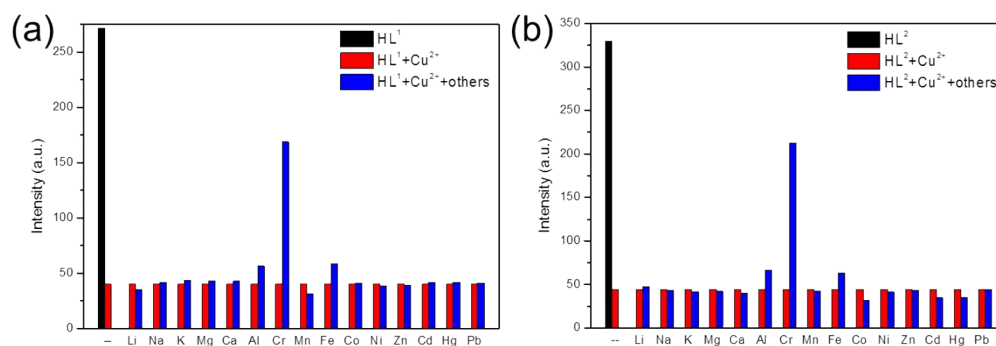


Figure S6 Fluorescence intensity of complexes of HL^1/ HL^2 and Cu^{2+} in the presence of various metal ions at 535 nm in THF/HEPES (3:7, v/v, pH = 7.4), excited by 435nm.

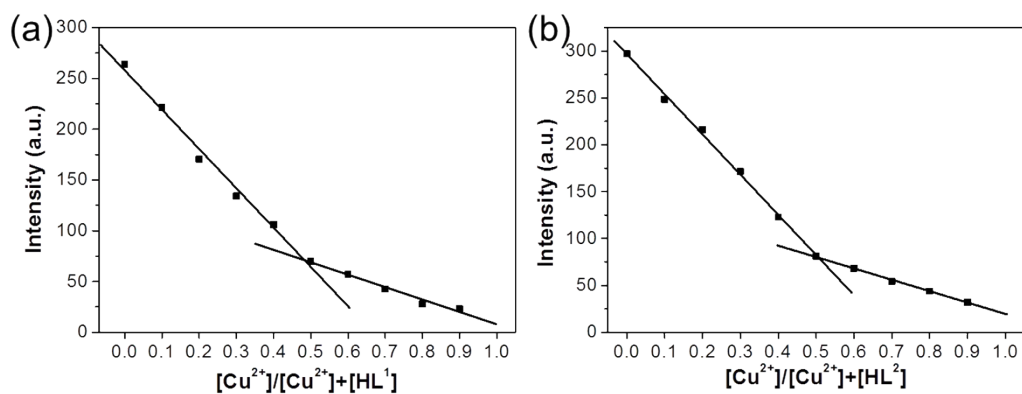


Figure S7 The Job's plots for the determination of the stoichiometry of Cu^{2+} : (a) HL^1 ,

(b) HL² in THF/HEPES (3:7, v/v, pH = 7.4).

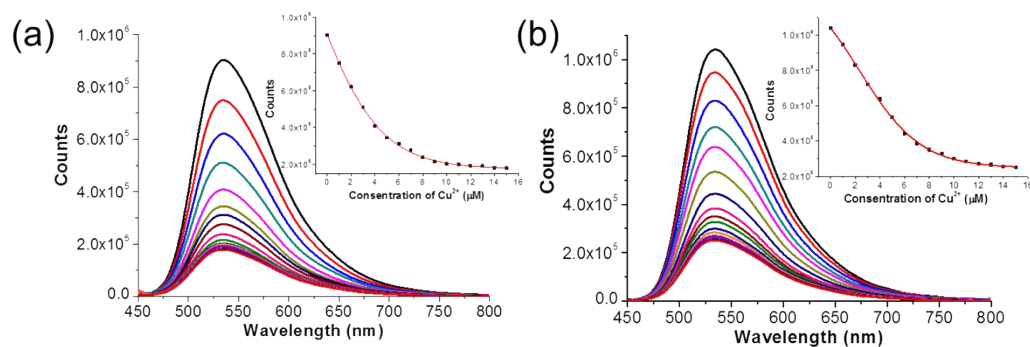


Figure S8 Changes of fluorescence spectra of 10 μM (a) HL¹, (b) HL² upon addition of Cu^{2+} ions in THF/HEPES (3:7, v/v, pH = 7.4), excited by 435nm. Inset: Fluorescence intensity at 535 nm as a function of $[\text{Cu}^{2+}]$.

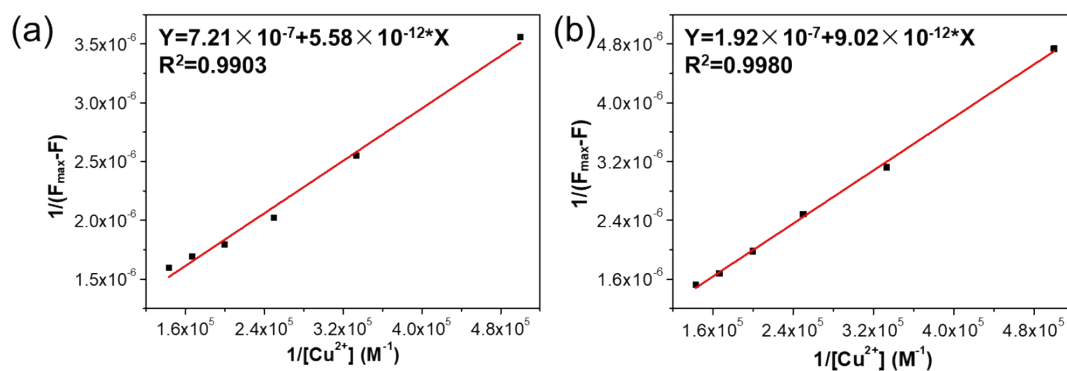


Figure S9 The linear relationship between $1 / (F_{\text{max}} - F)$ and $1 / [\text{Cu}^{2+}]$ in (a) HL¹ + Cu^{2+} system and (b) HL² + Cu^{2+} system.

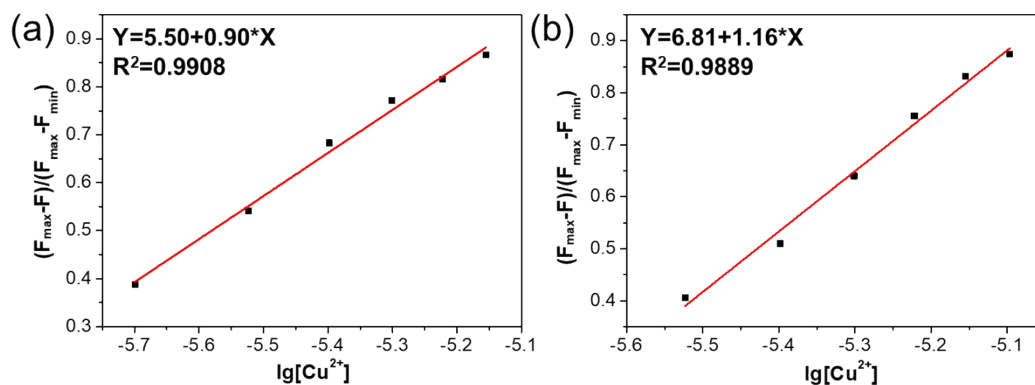


Figure S10 The linear relationship between $(F_{\max}-F) / (F_{\max}-F_{\min})$ and $\lg [Cu^{2+}]$ in (a) $HL^1 + Cu^{2+}$ system and (b) $HL^2 + Cu^{2+}$ system.

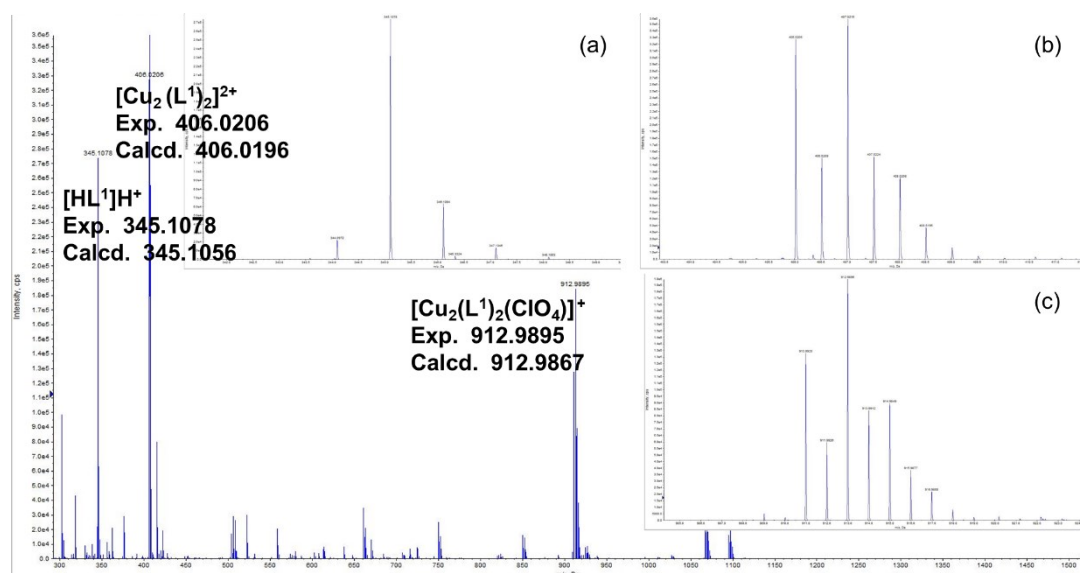


Figure S11 ESI-MS of HL^1 upon addition 1.0 equiv. of $Cu(ClO_4)_2$: (a), (b), (c) are isotopic peaks at m/z values of 345.1078, 406.0206, 912.9895, respectively.

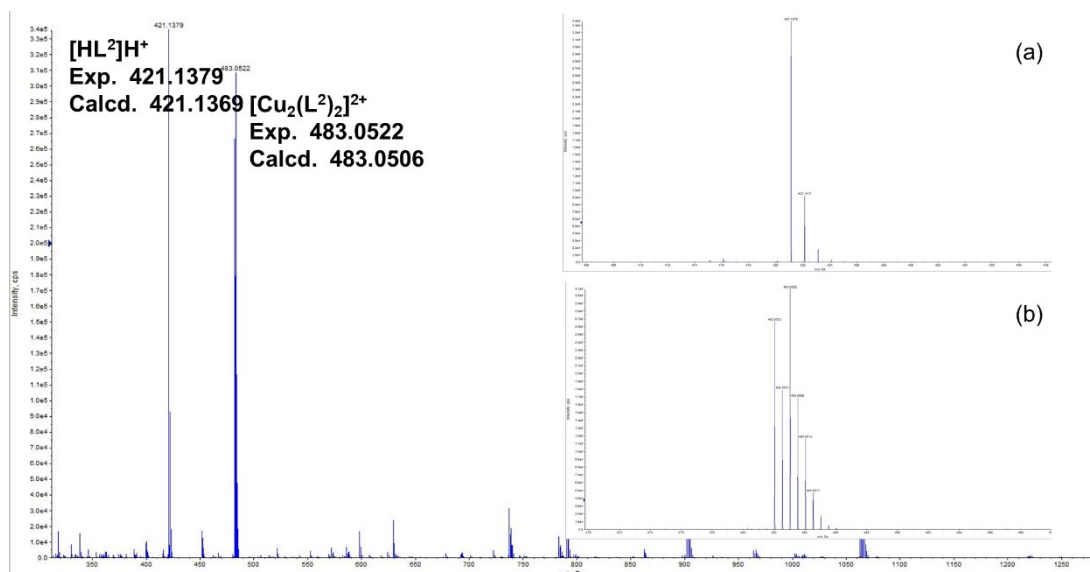


Figure S12 ESI-MS of HL^2 upon addition 1.0 equiv. of $Cu(ClO_4)_2$: (a), (b) are isotopic peaks at m/z values of 421.1379 and 483.0522, respectively.

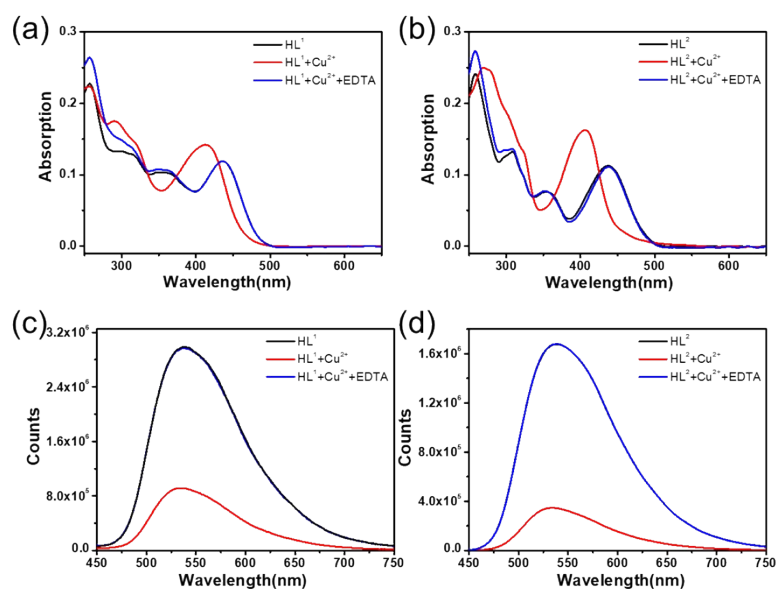


Figure S13 The absorption spectra of (a) HL^1 and (b) HL^2 (10 μM) before and after the equal addition of Cu^{2+} and EDTA in THF/HEPES (3:7, v/v, pH = 7.4). (c) The fluorescence spectra of (c) HL^1 and (d) HL^2 (10 μM) before and after the equal addition of Cu^{2+} and EDTA in THF/HEPES (3:7, v/v, pH = 7.4), excited by 435nm.

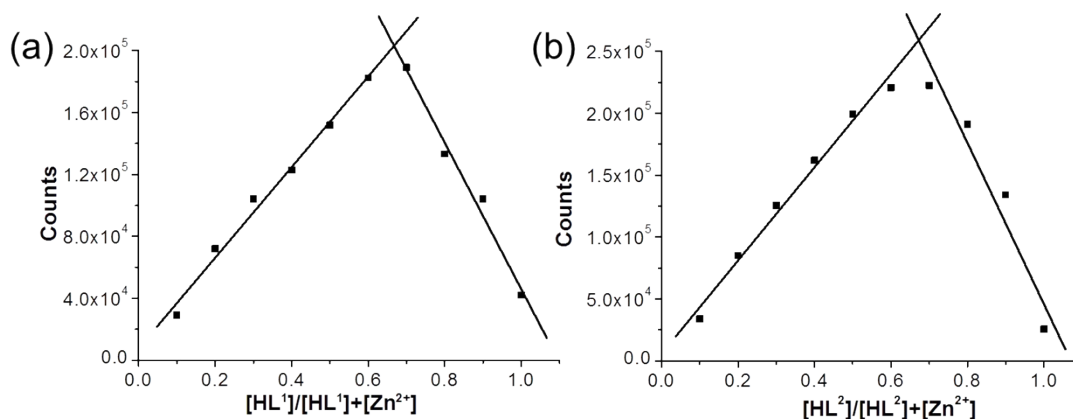


Figure S14 Job's plot for the determination of the stoichiometry of Zn^{2+} : (a) HL¹ and (b) HL² in EtOH/HEPES (9:1, v/v, pH = 7.4).

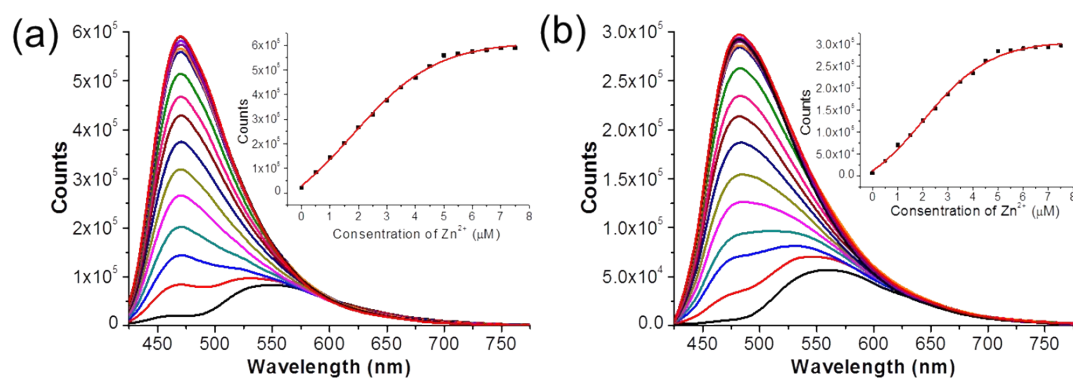


Figure S15 Changes of fluorescence spectra of 10 μ M (a) HL¹ and (b) HL² upon addition of Zn^{2+} ions in EtOH/HEPES (9:1, v/v, pH = 7.4), excited by 400nm and 410nm. Inset: Fluorescence intensity at 470 nm and 480nm as a function of $[Zn^{2+}]$.

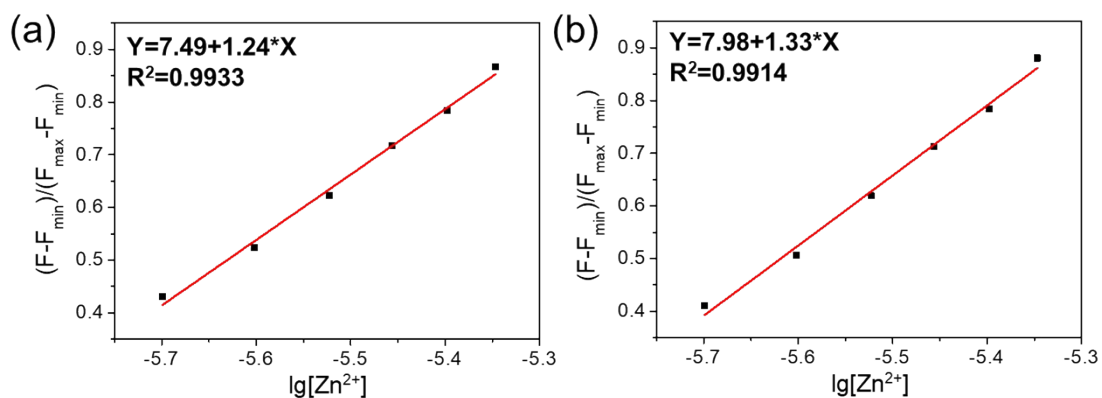


Figure S16 The linear relationship between $(F-F_{\min}) / (F_{\max}-F_{\min})$ and $\lg [Zn^{2+}]$ in (a) HL¹ + Zn²⁺ system and (b) HL² + Zn²⁺ system.

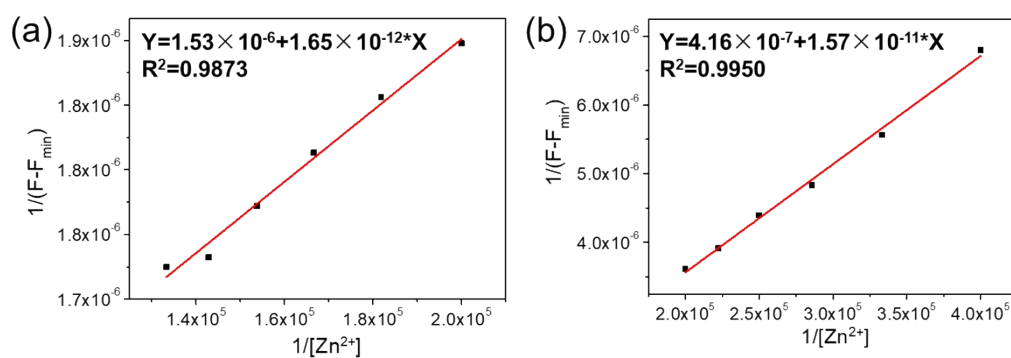


Figure S17 The linear relationship between $1 / (F-F_{\min})$ and $1 / [Zn^{2+}]$ in (a) HL¹ + Zn²⁺ system and (b) HL² + Zn²⁺ system.

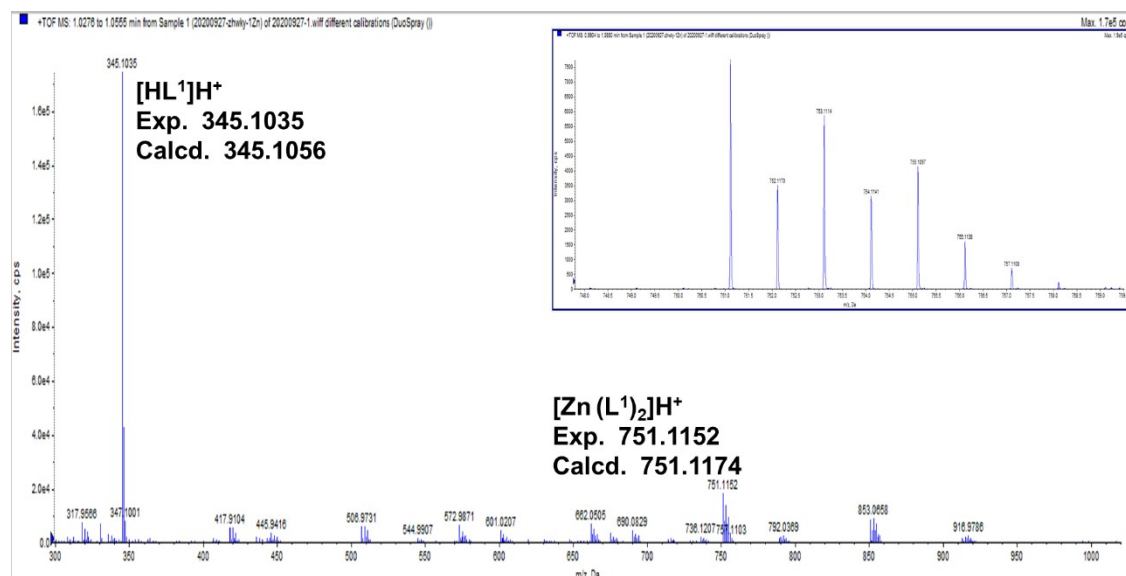


Figure S18 ESI-MS of HL¹ upon addition 1.0 equiv. of Zn(ClO₄)₂. Inset: Isotopic peaks at m / z values of 751.1152.

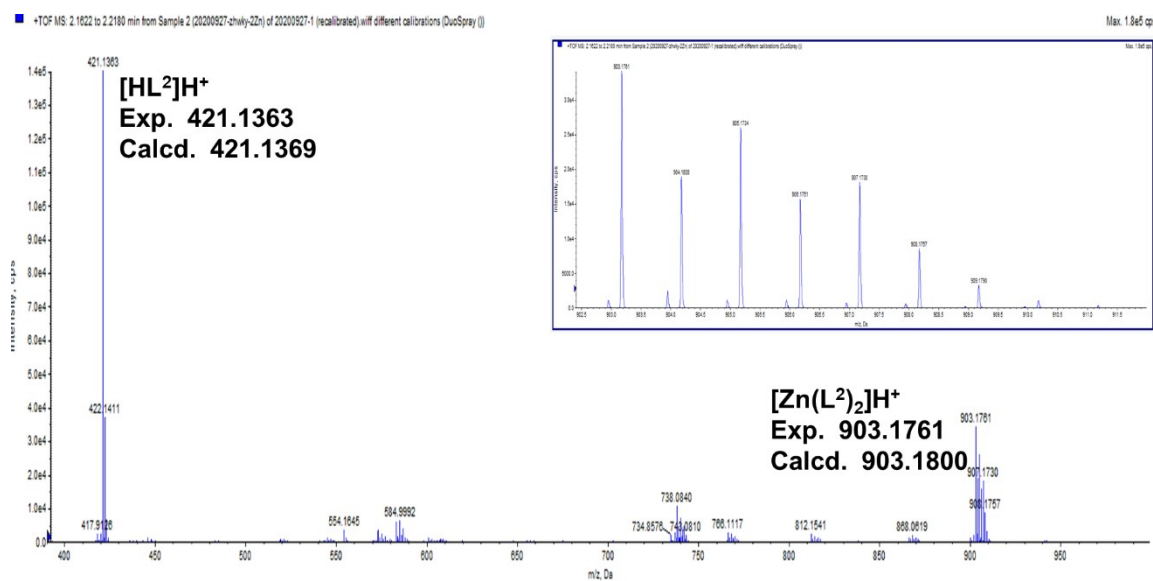


Figure S19 ESI-MS of HL² upon addition 1.0 equiv. of Zn(ClO₄)₂. Inset: Isotopic peaks at m / z values of 903.1761.

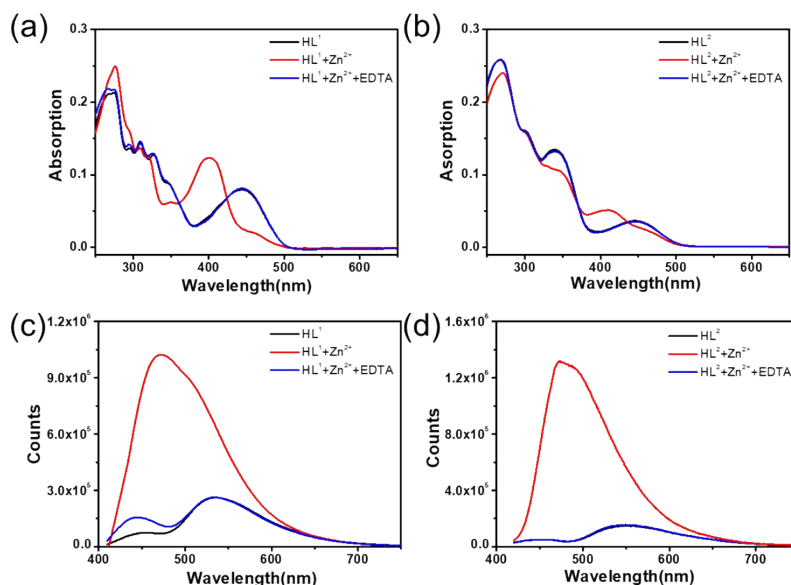


Figure S20 Absorption spectra of (a) HL^1 and (b) HL^2 (10 μ M) before and after the equal addition of Zn^{2+} and EDTA in EtOH/HEPES (9:1, v/v, pH = 7.4). (c) The fluorescence spectra of (c) HL^1 and (d) HL^2 (10 μ M) before and after the equal addition of Zn^{2+} and EDTA in EtOH/HEPES (9:1, v/v, pH = 7.4), excited by 400nm and 410nm, respectively.

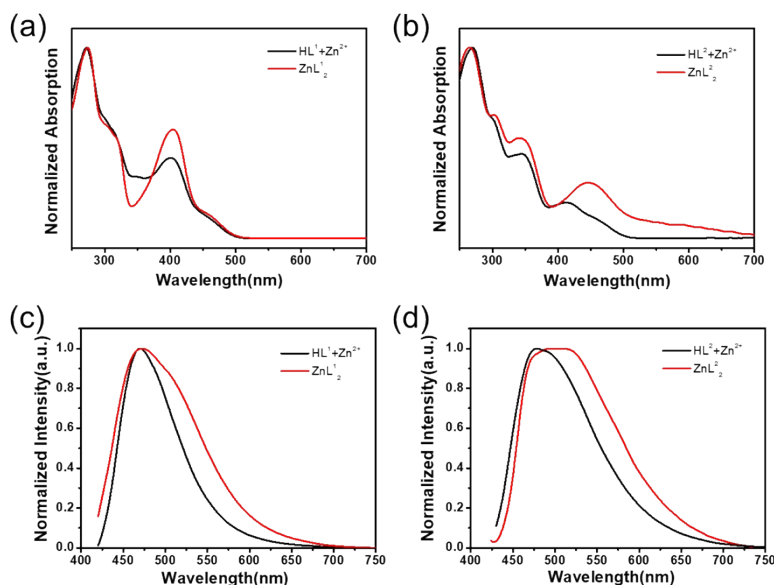


Figure S21 Absorption spectra of (a) $Zn-HL^1$, ZnL^1_2 and (b) $Zn-HL^2$, ZnL^2_2 (10 μ M) in EtOH/HEPES (9:1, v/v, pH = 7.4). (c) The fluorescence spectra of (c) $Zn-HL^1$, ZnL^1_2 and (d) $Zn-HL^2$, ZnL^2_2 (10 μ M) in EtOH/HEPES (9:1, v/v, pH = 7.4), excited by 400nm and 410nm, respectively.

Table S1. Crystal data and structure refinement parameters of HL¹, HL² and HL³.

	HL ¹	HL ²	HL ³
Empirical formula	C ₂₁ H ₁₆ N ₂ OS	C ₂₇ H ₂₀ N ₂ OS	C ₃₃ H ₂₄ N ₂ OS
Formula weight	344.42	420.51	496.60
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Pc</i>
Temperature (K)	150.00(10)	150.01(10)	150.00(10)
a (Å)	4.81310(10)	13.3315(2)	7.4154(2)
b (Å)	22.3451(3)	6.79410(10)	12.5669(2)
c (Å)	15.3199(2)	23.9317(3)	13.4796(2)
α (°)	90	90	90
β (°)	93.7770(10)	104.2320(10)	95.107(2)
γ (°)	90	90	90
V(Å ³)	1644.06(5)	2101.10(5)	1251.16(4)
Z	4	4	2
D _c (g cm ⁻³)	1.391	1.329	1.318
μ (mm ⁻¹)	1.829	1.535	1.375
F(000)	720.0	880.0	520.0
Radiation	Cu K _α	Cu K _α	Cu K _α
2θ range(°)	7.006 to 151.252	6.84 to 144.134	7.034 to 143.948
R(int)	0.0380	0.0207	0.0225
R ₁ , wR ₂ [I > 2(I)]	0.0423, 0.1112	0.0302, 0.0796	0.0281, 0.0718
R ₁ , wR ₂ (all data)	0.0452, 0.1145	0.0331, 0.0818	0.0289, 0.0726
CCDC number	2046924	2046925	2046926

Table S2. Crystal data and structure refinement parameters of ZnL¹₂ and ZnL²₂.

	ZnL ¹ ₂	ZnL ² ₂
Empirical formula	C ₄₂ H ₃₀ N ₄ O ₂ S ₂ Zn	C ₅₄ H ₃₈ N ₄ O ₂ S ₂ Zn
Formula weight	752.260	904.457
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	99.99(10)	100.00(12)
a (Å)	9.16130(17)	22.0411(3)
b (Å)	14.4849(3)	10.85114(13)
c (Å)	14.8515(3)	17.7456(2)
α (°)	118.3611(19)	90
β (°)	94.9008(16)	105.2506(13)
γ (°)	96.0026(15)	90
V(Å ³)	1704.06(6)	4094.76(9)
Z	2	4
D _c (g cm ⁻³)	1.466	1.467

μ (mm ⁻¹)	2.504	2.190
F(000)	776.2	1873.3
Radiation	Cu K α	Cu K α
2 θ range(°)	6.84 to 152.98	8.32 to 153.58
R(int)	0.0420	0.0402
R ₁ , wR ₂ [I > 2(I)]	0.0351, 0.0945	0.0678, 0.1679
R ₁ , wR ₂ (all data)	0.0372, 0.0964	0.0745, 0.1740
CCDC number	2055758	2055759

Table S3. Selected Bond Distanced (Å) and Angles (deg) for ZnL¹₂ and ZnL²₂.

ZnL¹₂			
Zn1-N4	2.0006(14)	Zn1-N2	2.0080(14)
Zn1-O1	1.9308(12)	Zn1-O2	1.9428(12)
O1-Zn1-N4	109.97(6)	O2-Zn1-N4	94.24(5)
N2-Zn1-N4	127.70(6)	O2-Zn1-O1	124.30(5)
N2-Zn1-O1	95.06(5)	O2-Zn1-N2	108.65(6)
ZnL²₂			
Zn1-N4	2.016(3)	Zn1-N2	2.044(4)
Zn1-O1	1.920(2)	Zn1-O2	1.949(3)
O1-Zn1-N4	115.22(11)	O2-Zn1-N4	95.49(12)
N2-Zn1-N4	125.97(15)	O2-Zn1-O1	116.09(11)
N2-Zn1-O1	94.98(13)	O2-Zn1-N2	110.52(17)

Reference

- [1] I. J. Chang, K. S. Hwang and S. K. Chang, *Dye. Pigment.*, 2017, **137**, 69–74.