Electronic Supplementary Material (ESI) for RSC Advances.

Fluorescence response of a thiazolidine carboxylic acid derivative for the selective and nanomolar detection of Zn(II) ions: quantum chemical calculations and application in real samples

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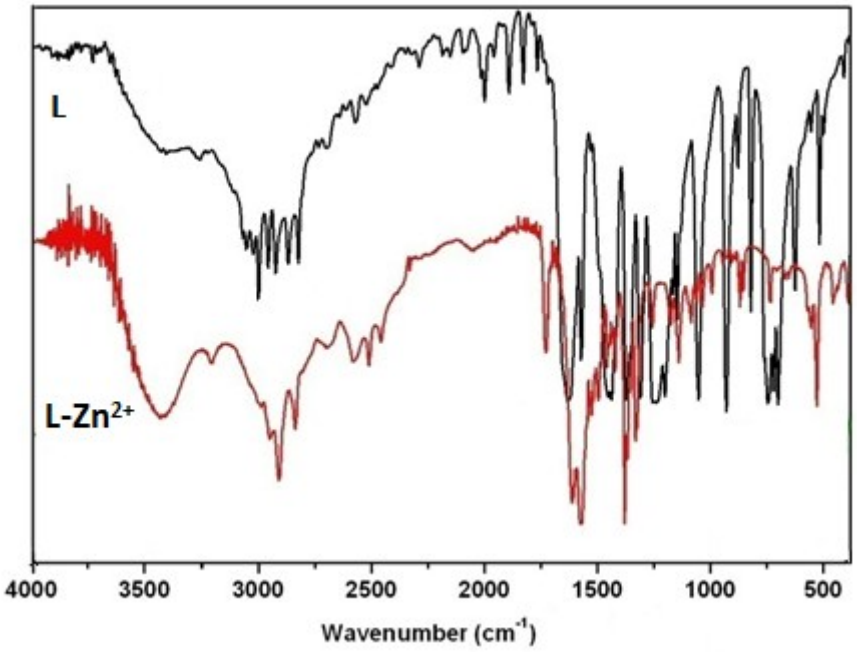


Fig. S1 FT-IR spectra of L and L-Zn^{2+}.

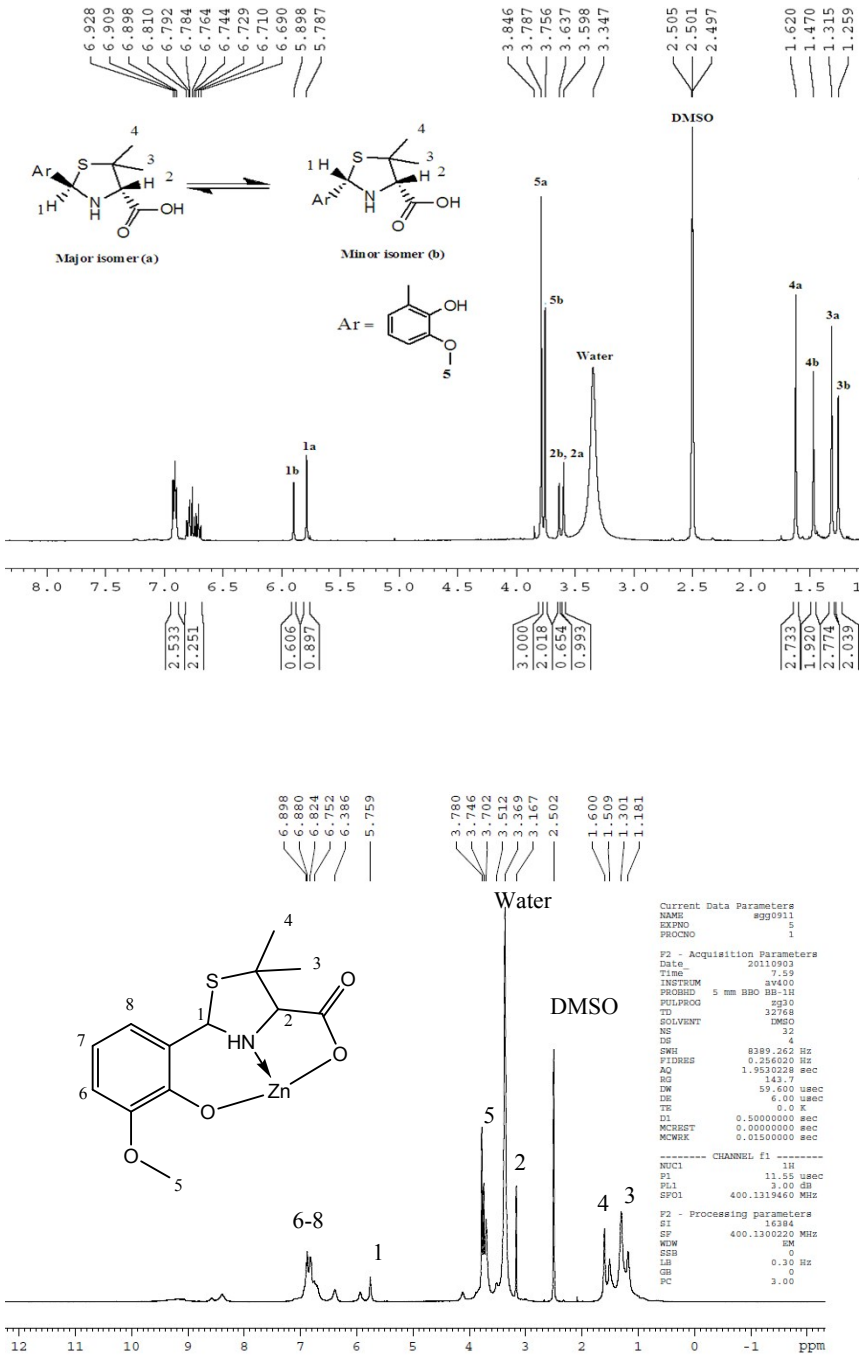


Fig. S2 ^{1}H-NMR spectrum of L and L-Zn^{2+}

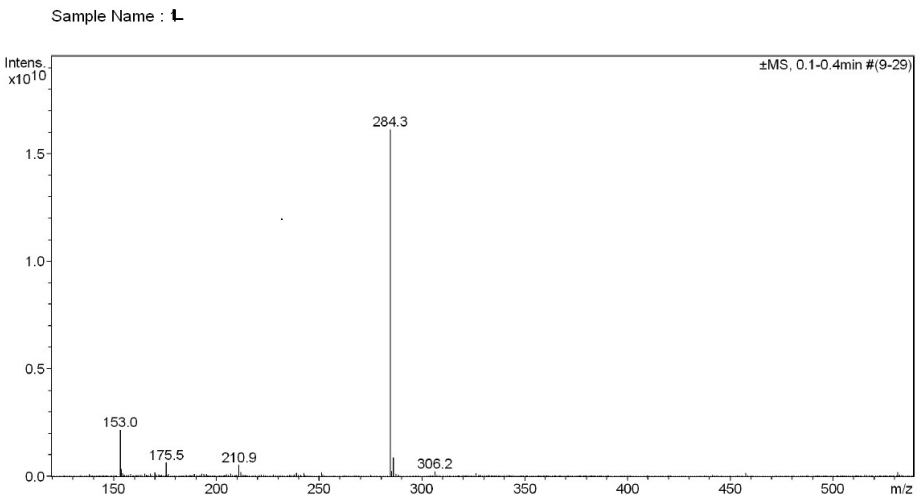


Fig. S3 ESI- MS spectrum of L.

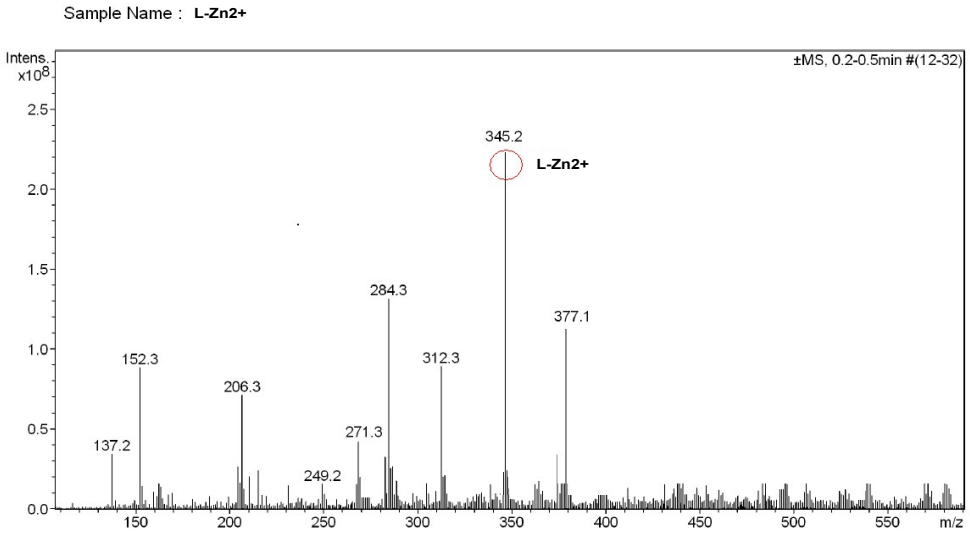


Fig. S4 ESI- MS spectrum of L-Zn^{2+}.

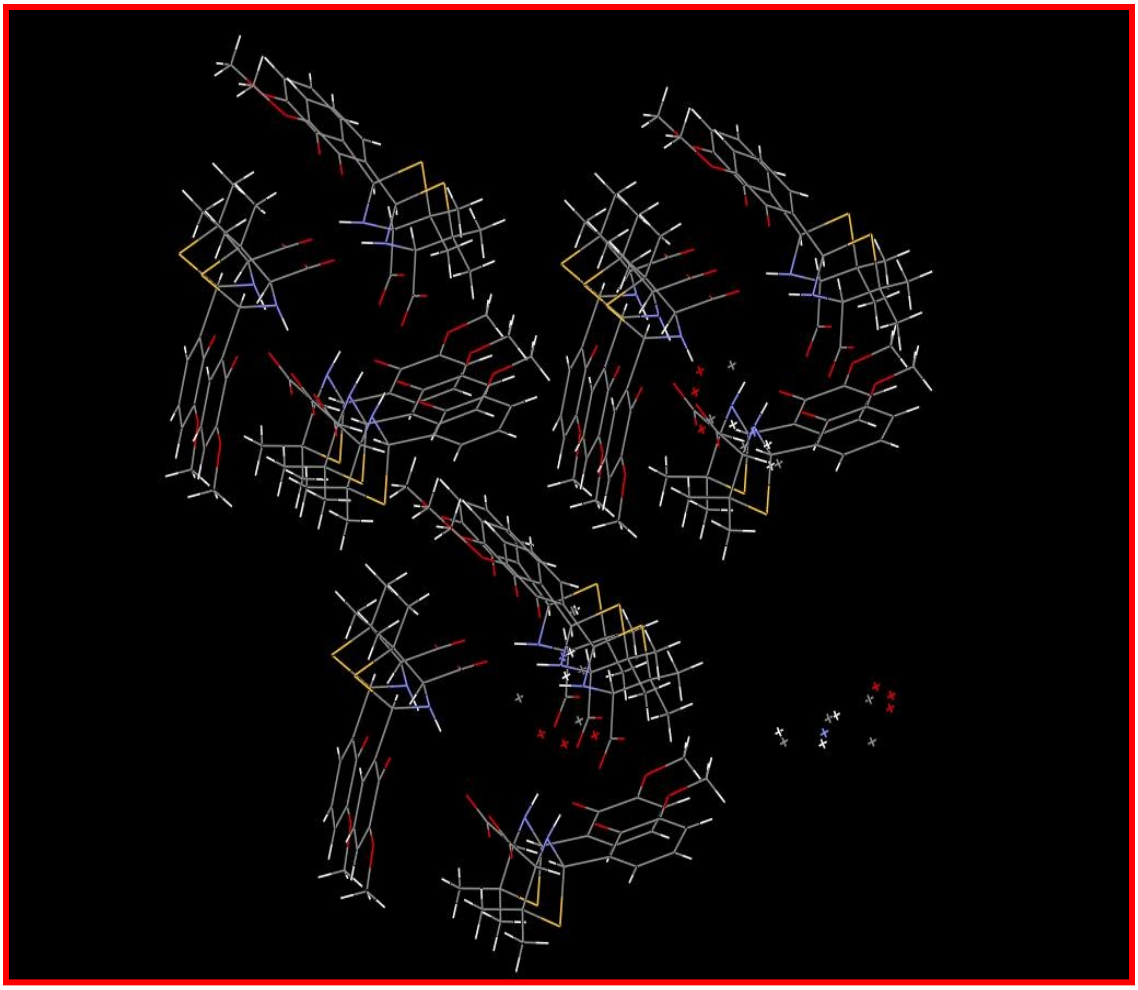


Fig. S5 Crystal packing diagram of L (*b*-axis)

Evaluation of association constant (K_a)

By UV-visible method

The association constants for the formation of the L-Zn^{2+} complex were evaluated using the Benesi-Hildebrand (B-H) plot.

$$1/(A\text{-}A_o) = 1/\{K(A_{max}–A_o)\ [M^{x+}]^n\} + 1/[A_{max}–A_o]$$

Where A_o is the absorbance of L in the absence of Zn^{2+}, A is the absorbance of L in the presence of Zn^{2+}, A_{max} is absorbance in presence of added $[M^{x+}]_{max}$ and K_a is the association constant, where $[M^{X+}]$ is $[Zn^{2+}]$. The association constant (K_a) could be determined from the slope of the straight line of the plot of $1/(A\text{-}A_o)$ Vs. $1/[Zn^{2+}]$ and is found to be 5.26×10^5 M^{-1}.

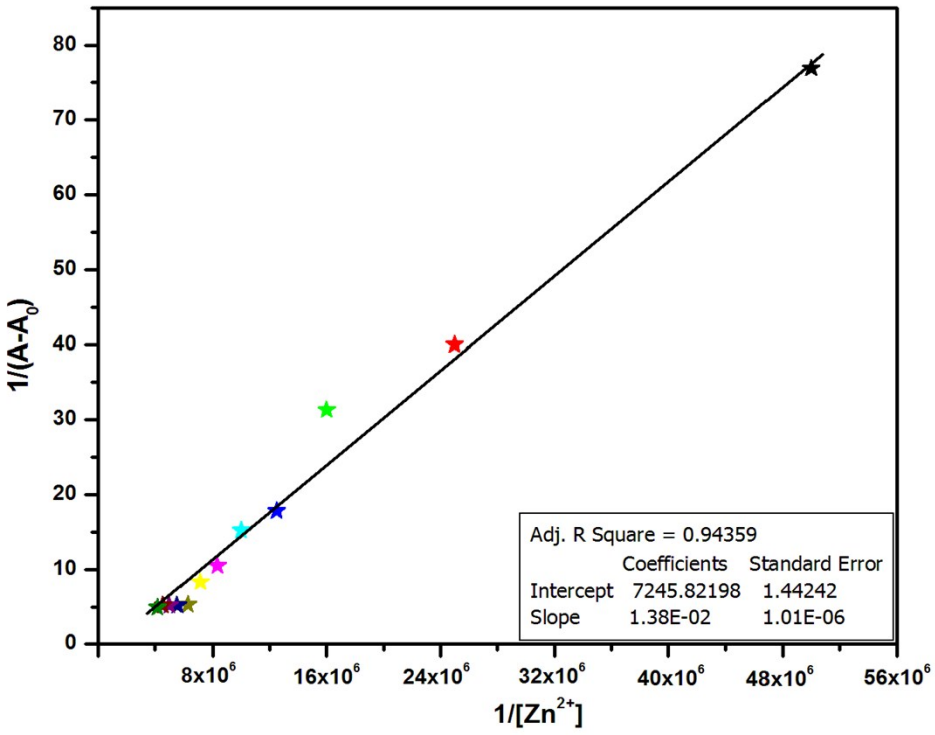


Fig. S6 Benesi-Hildebrand plot from UV-vis titration data of with Zn^{2+} concentration.

Calculation of quantum yield

The fluorescence quantum yield (Φ_x) for L and L.Zn^{2+} was measured at room temperature using standard solutions of fluorescien $(\Phi_x = 0.79)$ in 95 % (v/v) water-methanol mixture at an excitation wavelength 441 nm. The quantum yield was determined by the following eqn,

$$\Phi_x = \Phi_{st} \bullet (A_{st}/A_x) \bullet (F_x/F_{st}) \bullet (n_x^2/n_{st}^2) \bullet (D_x/D_{st})$$

Where, Φ_x is the quantum yield of the sample, Φ_{st} is the quantum yield of the reference, A_x and A_{st} are the absorbances of the sample and the reference, F_x and F_{st} are the areas of emission for the sample and the reference, n_x^2 and n_{st}^2 are the refractive indices of the solvents and D_x and D_{st} is the dilution factor of the sample and reference respectively.

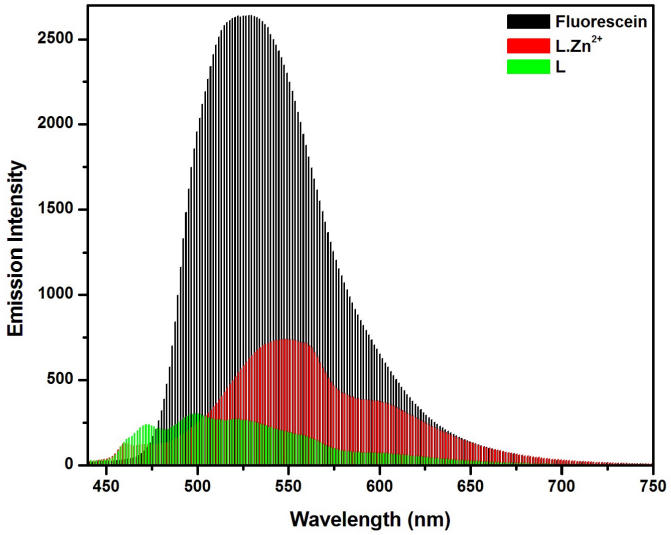


Fig. S7 Emission spectrom of L, L-Zn^{2+} and fluorescien in 95 % (v/v) water-methanol mixture.

Calculation:

For Zn^{2+}

$\Phi_{st} = 0.79$, $A_{st} = 441$ nm, $A_x = 375$ nm, $F_x = 70728.7$, $F_{st} = 226711.1$, $(n) = 1.3284$, $D_x = 0.002$ and $D_{st} = 0.003$

$$\Phi_x = 0.79 \bullet (441/375) \bullet (70728.7/226711.1) \bullet (1.3284/1.3284) \bullet (0.002/0.003)$$

$$\Phi_x = 0.19$$

For L

$\Phi_{st} = 0.79$, $A_{st} = 441$ nm, $A_x = 285$ nm, $F_x = 70728.7$, $F_{st} = 226711.1$, $(n) = 1.3284$, $D_x = 0.002$ and $D_{st} = 0.003$

$$\Phi_x = 0.79 \bullet (441/285) \bullet (27169.3/226711.1) \bullet (1.3284/1.3284) \bullet (0.002/0.003)$$

$$\Phi_x = 0.09$$

By fluorescence method

Also the binding constant value of Zn^{2+} with L has been determined by fluorescence spectroscopy method using the modified Benesi-Hildebrand equation,

$$1/\Delta I = 1/\Delta I_{max} + (1/K_a[C])\ (1/\Delta I_{max})$$

Here $\Delta I = I - I_{min}$ and $\Delta I_{max} = I_{max} - I_{min}$

Where I_{min} is the emission intensities of L in the absence of Zn^{2+}, I is the intermediate Zn^{2+} concentration, I_{max} is the concentration of complete saturation, K_a is the binding constant and [C] is the concentration of Zn^{2+}respectively. From the plot of $[1/(I - I_{min})]$ Vs $[C]^{-1}$ for L, the binding value of K_a has been determined from the slope and is found to be 2.48×10^5 M^{-1}.

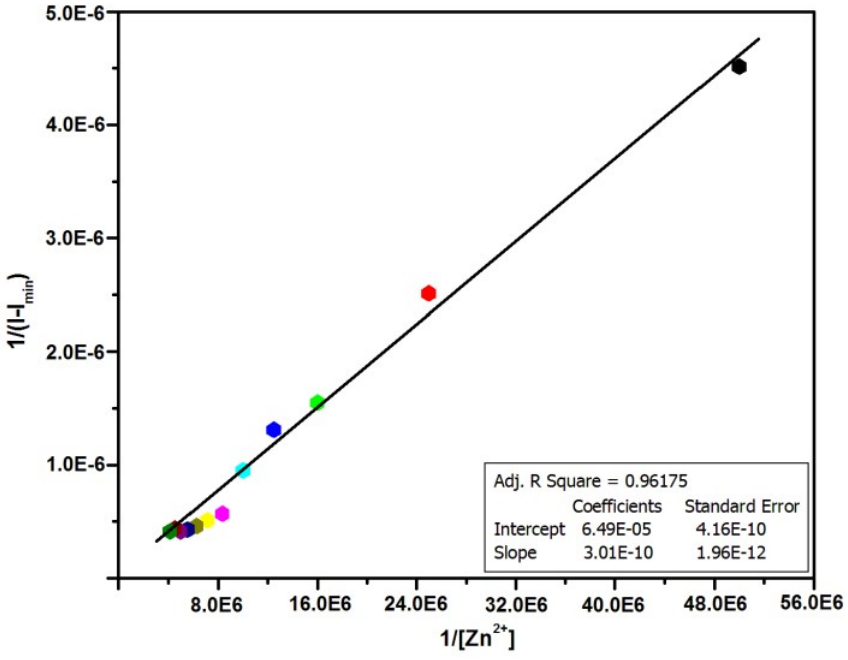


Fig. S8 Benesi-Hildebrand plot from fluorescence titration data of L (10.0 μM) with Zn^{2+} (0-3 eq.).

Job plot measurements

The ligand L (5.6 mg, 0.01M) was dissolved in 95 % (v/v) water-methanol mixture (2 mL). 100, 90, 80, 70, 60, 50, 40, 30, 20, 10 and 0 µL of the solution of L were taken and transferred to 5.0 ml bottles. Each bottle was diluted with water to make a total volume of 3.0 ml. Metal ion Zn^{2+} (0.01M) was dissolved in water. 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 µL of the Zn^{2+} solution were added to each diluted solution of L. Each bottle had a total volume of 5.0 ml. After shaking them for few minutes, emission spectra were taken at room temperature.

Job's plots were drawn by plotting $\Delta I.X_h$ vs. X_h (ΔI = change of absorbance of the absorption spectrum at 375 nm during titration and X_h is the mole fraction of host in each case, respectively).

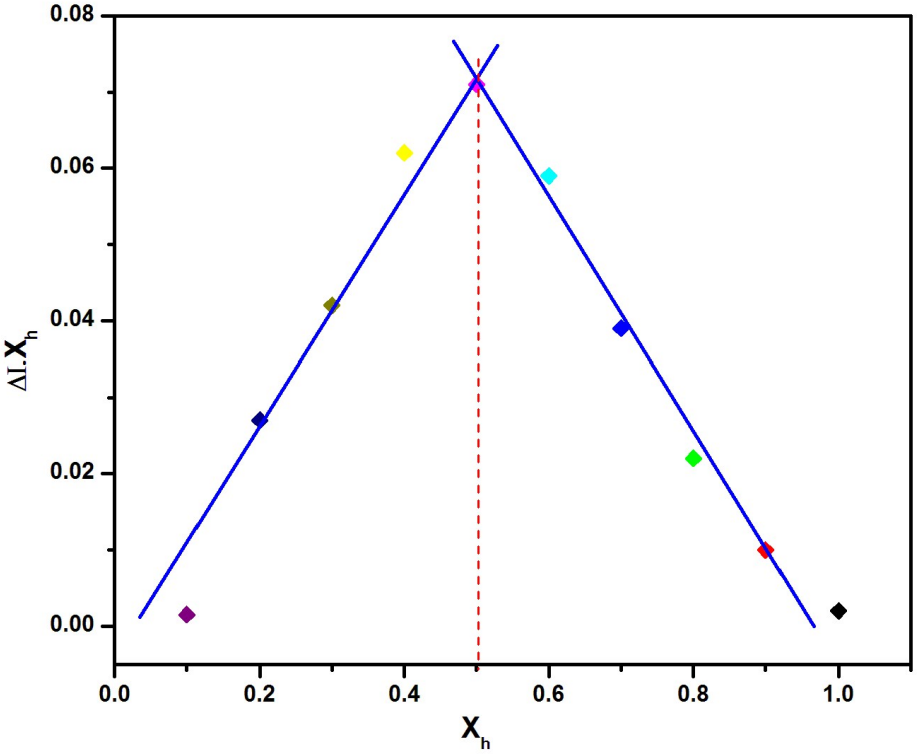


Fig. S9 Job's plot diagram of L for Zn^{2+} (where X_h is the mole fraction of $Zn^{2+}$and ΔI indicates the change of absorbance at 375 nm).

Detection limit for Zn^{2+} ions

The detection limit was calculated based on the emission titration. The emission spectrum of L was measured 10 times and the standard deviation of blank measurements was determined. To gain the slope, the ratio of the emission at λ_{max} 481 nm was plotted vs. the concentration of Zn^{2+} ions. The detection limit was measured using the following equation,

$$\text{Detection Limit (DL)} = 3\sigma/k$$

Where, σ is standard deviation of blank measurement.

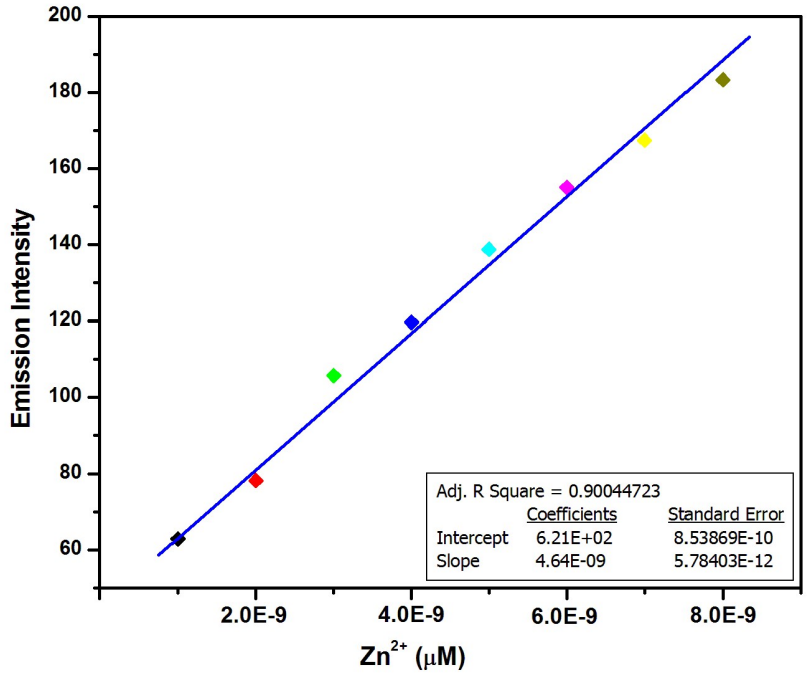
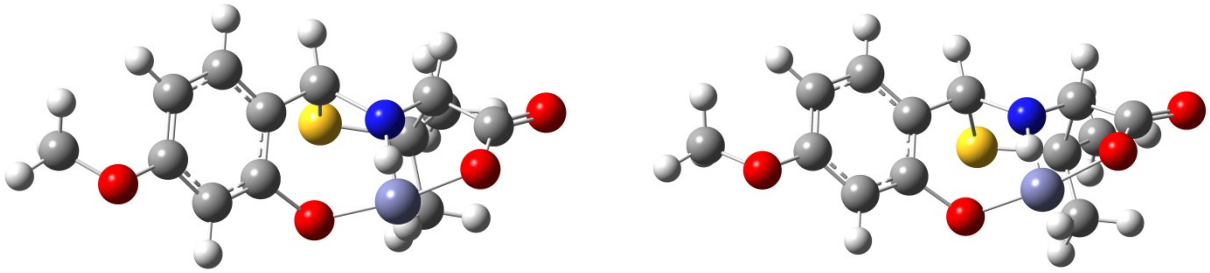


Fig. S10 Emission of L at 481 nm depending on the concentration of Zn^{2+}.



(a) **(b)**

Fig. S11 Optimized structure of L-Zn^{2+} complex in (a) ground and (b) excited state.

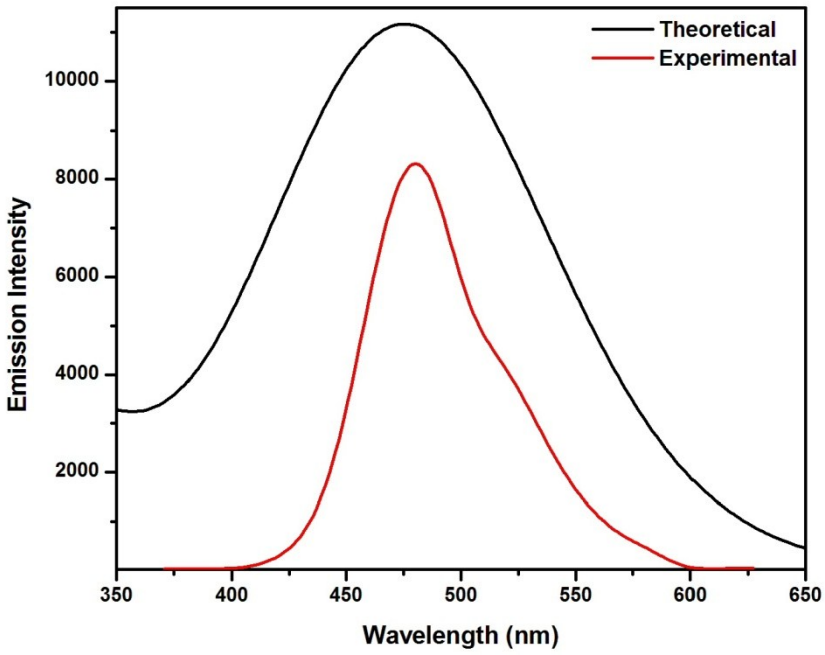


Fig. S12 Calculated and experimental emission spectra of L-Zn^{2+}.

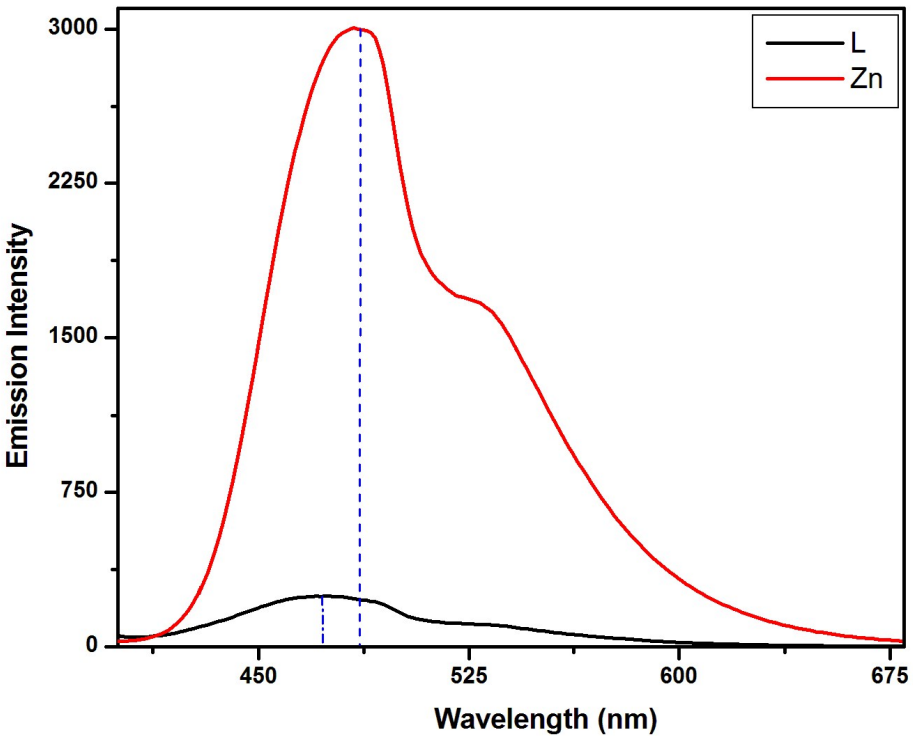


Fig. S13 Emission spectra of L and L-Zn^{2+}.

Table S1 Comparison of reported detection limit of zinc ion sensors with the present work.

Compounds	Detection limit (M)	Analyte	Response	References
2-((1H-1,2,4-triazol-3-ylimino)methyl)-4-methoxy phenol	1.70×10^{-7}	Zn^{2+}	Enhancement	25a
4-(4-hydroxy-3-methoxybenzylideneamino)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one	1.00×10^{-7}	Zn^{2+}	Enhancement	25b
2-(1-(naphthalen-1-yl)-1Htetrazol-5-yl) quinolone	2.00×10^{-8}	Zn^{2+}	Enhancement	25c
(E)-2-(2-hydroxy-3-methoxybenzylideneamino)-3-(1H-indol-3-yl) propanoic acid	1.04×10^{-8}	Zn^{2+}	Enhancement	25d
2,4-di-tert-butyl-6-[(1-hydroxycyclohexylmethyl imino)methyl]phenol	7.25×10^{-7}	Zn^{2+}	Enhancement	25e
N,N′,N″-tris(salicylidene)(2-aminoethyl) amine	1.10×10^{-6}	Zn^{2+}	Enhancement	25f
Tris(3-(2-hydroxyacetophenone)propyl)amine	8.80×10^{-8}	Zn^{2+}	Enhancement	25g
2-(2-hydroxy-4-methoxyphenyl)-5,5-dimethyl-1,3-thiazolidine-4-carboxylic acid	13.90×10^{-9}	Zn^{2+}	Enhancement	Present work

Table S2 Successive protonation constants (log K_{LHx}) and dissociation constants (pK) of L and stability constant (log β_{ZnL}) of L-Zn^{2+} system at I = 0.15 M $NaClO_4$ and temperature 310 K. Standard deviations are given in parentheses.

Parameters	L	pK	L-Zn^{2+}
log K_{LH}	10.93(3)	10.93 (-OH)	--
log K_{LH2}	17.27(6)	6.34 (for thiazolidine nitrogen)	--
log K_{LH3}	20.06(4)	2.79 (-COOH)	--
log β_{ZnL}	-		11.33

Table S3 Experimental bond lengths (Å) and angles (◦) for L

Parameters	Bond lengths (Å)	Parameters	Bond angles (◦)	Parameters	Torsion angles (◦)
C(4)-O(2)	1.350(6)	O(2)-C(4)-C(3)	124.5(5)	C(2)-C(3)-C(4)-O(2)	-179.1(5)
C(5)-O(1)	1.355(5)	O(2)-C(4)-C(5)	115.2(4)	O(2)-C(4)-C(5)-O(1)	0.700(7)
C(9)-S(1)	1.817(5)	O(1)-C(5)-C(6)	119.9(5)	C(3)-C(4)-C(5)-O(1)	-178.8(5)
C(7)-N(1)	1.500(13)	O(1)-C(5)-C(4)	120.6(4)	O(2)-C(4)-C(5)-C(6)	178.9(5)
C(7)-S(1)	1.831(13)	C(8)-C(9)-S(1)	108.0(5)	O(1)-C(5)-C(6)-C(1)	178.3(5)
C(8)-N(1)	1.493(12)	C(11)-C(9)-S(1)	108.3(4)	C(1)-C(6)-C(7)-N(1)	65.2(11)
N(1)-H(1A)	0.85(2)	N(1)-C(7)-C(6)	114.9(9)	C(5)-C(6)-C(7)-N(1)	-104.4(9)
O(4)-C(13)	1.27(2)	N(1)-C(7)-S(1)	110.1(8)	C(1)-C(6)-C(7)-S(1)	-57.4(8)
O(3)-C(13)	1.134(17)	C(6)-C(7)-S(1)	107.1(8)	C(5)-C(6)-C(7)-S(1)	132.9(6)
C(7)-N(1)	1.500(13)	N(1)-C(8)-C(9)	101.5(7)	C(10)-C(9)-C(8)-N(1)	-79.9(8)
		N(1)-C(8)-C(13)	115.5(11)	C(11)-C(9)-C(8)-N(1)	163.3(7)
		C(9)-C(8)-C(13)	120.5(10)	S(1)-C(9)-C(8)-N(1)	49.7(8)
		C(8)-N(1)-C(7)	111.5(8)	N(1)-C(7)-S(1)-C(9)	19.7(8)
		C(8)-N(1)-H(1A)	123(7)	C(6)-C(7)-S(1)-C(9)	145.3(6)
		O(3)-C(13)-O(4)	127.0(15)	N(1)-C(8)-C(13)-O(3)	30.5(19)
		O(3)-C(13)-C(8)	117.3(16)		

Symmetry codes: i) –x+y, –x, z; ii) –y, x–y, z

Table S4 Calculated bond lengths (Å) and angles (◦) for L.

Parameters	Bond lengths (Å)	Parameters	Bond angles (◦)	Parameters	Torsion angles (◦)
C(4)-O(2)	1.39804	O(2)-C(4)-C(3)	127.10	C(2)-C(3)-C(4)-O(2)	-179.71
C(5)-O(1)	1.38063	O(2)-C(4)-C(5)	112.11	O(2)-C(4)-C(5)-O(1)	0.4790
C(9)-S(1)	1.85423	O(1)-C(5)-C(6)	121.24	C(3)-C(4)-C(5)-O(1)	-179.85
C(7)-N(1)	1.45129	O(1)-C(5)-C(4)	118.83	O(2)-C(4)-C(5)-C(6)	179.89
C(7)-S(1)	1.93478	C(8)-C(9)-S(1)	103.75	O(1)-C(5)-C(6)-C(1)	179.60
C(8)-N(1)	1.45458	C(11)-C(9)-S(1)	109.78	C(1)-C(6)-C(7)-N(1)	67.297
N(1)-H(1A)	1.02309	N(1)-C(7)-C(6)	112.46	C(5)-C(6)-C(7)-N(1)	-116.10
O(4)-C(13)	1.38028	N(1)-C(7)-S(1)	105.98	C(1)-C(6)-C(7)-S(1)	-59.951
O(3)-C(13)	1.22502	C(6)-C(7)-S(1)	112.01	C(5)-C(6)-C(7)-S(1)	134.64
C(7)-N(1)	1.45129	N(1)-C(8)-C(9)	109.89	C(10)-C(9)-C(8)-N(1)	-81.125
		N(1)-C(8)-C(13)	108.41	C(11)-C(9)-C(8)-N(1)	167.921
		C(9)-C(8)-C(13)	109.77	S(1)-C(9)-C(8)-N(1)	52.851
		C(8)-N(1)-C(7)	111.14	N(1)-C(7)-S(1)-C(9)	22.372
		C(8)-N(1)-H(1A)	112.48	C(6)-C(7)-S(1)-C(9)	155.36
		O(3)-C(13)-O(4)	123.12	N(1)-C(8)-C(13)-O(3)	47.903
		O(3)-C(13)-C(8)	126.04		

Table S5 Calculated bond lengths (Å) and angles (◦) for L-Zn^{2+} in ground state (GS).

Parameters	Bond lengths (Å)	Parameters	Bond angles (◦)	Parameters	Torsion angles (◦)
C(7)-N(1)	1.41013	C(7)-N(1)-C(8)	115.01	N(1)-C(8)-C(13)-O(3)	35.21
C(8)-N(1)	1.45154	C(7)-N(1)-Zn(1)	119.23	C(5)-C(6)-C(7)-N(1)	0.720
C(13)-O(3)	1.27952	N(1)-Zn(1)-O(3)	82.929	O(1)-Zn(1)-N(1)-C(7)	13.97
C(13)-O(4)	1.36112	C(8)-N(1)-Zn(1)	115.82	C(8)-N(1)-Zn(1)-O(3)	20.15
C(9)-S(1)	2.95362	C(8)-C(13)-O(3)	123.98	C(8)-N(1)-C(7)-S(1)	43.09
C(7)-S(1)	2.22821	C(13)-O(3)-Zn(1)	107.67	C(8)-C(9)-S(1)-C(7)	0.353
O(1)-C(5)	1.41452	O(1)-Zn(1)-N(1)	106.07	C(3)-C(4)-O(2)-C(12)	1.590
O(2)-C(4)	1.40011	O(1)-C(5)-C(4)	115.99	O(2)-C(4)-C(5)-O(1)	0.685
O(3)-Zn(1)	2.25247	C(8)-C(13)-O(4)	117.13	O(1)-C(5)-C(6)-C(7)	1.391
O(1)-Zn(1)	1.86901	C(3)-C(4)-O(2)	123.85	C(6)-C(7)-N(1)-Zn(1)	26.95
N(1)-Zn(1)	1.93714	C(6)-C(5)-O(1)	127.01	C(10)-C(9)-C(8)-N(1)	186.19

Table S6 Calculated bond lengths (Å) and angles (◦) for L-Zn^{2+}in excited state (ES).

Parameters	Bond lengths (Å)	Parameters	Bond angles (◦)	Parameters	Torsion angles (◦)
C(7)-N(1)	1.40931	C(7)-N(1)-C(8)	114.16	N(1)-C(8)-C(13)-O(3)	34.17
C(8)-N(1)	1.44366	C(7)-N(1)-Zn(1)	118.96	C(5)-C(6)-C(7)-N(1)	45.29
C(13)-O(3)	1.27486	N(1)-Zn(1)-O(3)	82.447	O(1)-Zn(1)-N(1)-C(7)	13.07
C(13)-O(4)	1.35590	C(8)-N(1)-Zn(1)	115.14	C(8)-N(1)-Zn(1)-O(3)	19.96
C(9)-S(1)	2.81711	C(8)-C(13)-O(3)	123.46	C(8)-N(1)-C(7)-S(1)	42.89
C(7)-S(1)	2.12126	C(13)-O(3)-Zn(1)	107.41	C(8)-C(9)-S(1)-C(7)	0.394
O(1)-C(5)	1.37781	O(1)-Zn(1)-N(1)	105.95	C(3)-C(4)-O(2)-C(12)	1.510
O(2)-C(4)	1.39812	O(1)-C(5)-C(4)	115.34	O(2)-C(4)-C(5)-O(1)	0.691
O(3)-Zn(1)	2.11887	C(8)-C(13)-O(4)	116.39	O(1)-C(5)-C(6)-C(7)	1.294
O(1)-Zn(1)	1.86308	C(3)-C(4)-O(2)	123.56	C(6)-C(7)-N(1)-Zn(1)	25.98
N(1)-Zn(1)	1.92283	C(6)-C(5)-O(1)	126.50	C(10)-C(9)-C(8)-N(1)	171.21