Supplementary data file

Three-in-one type fluorescent sensor based on pyrene pyridoxal cascade for the selective detection of Zn(II), hydrogen phosphate and cysteine

Yachana Upadhyay[a,Φ], Thangaraj Anand[a,Φ], Lavanya Thilak Babu[b], Priyankar Paira[b], Guido Crisponi[c], Ashok Kumar SK[d], Rajender Kumar[a] and Suban K Sahoo[a,*]

[a] *Department of Applied Chemistry, SV National Institute of Technology (SVNIT), Surat-395007, India. (E-mail: suban_sahoo@rediffmail.com; Tel.: 91-261-2201855)*

[b] *Pharmaceutical Chemistry Division, School of Advanced Sciences, VIT University, Vellore-632014, India.*

[c] *Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, 09042 Monserrato, Italy.*

[d] *Materials Chemistry Division, School of Advanced Sciences, VIT University, Vellore-632014, India.*

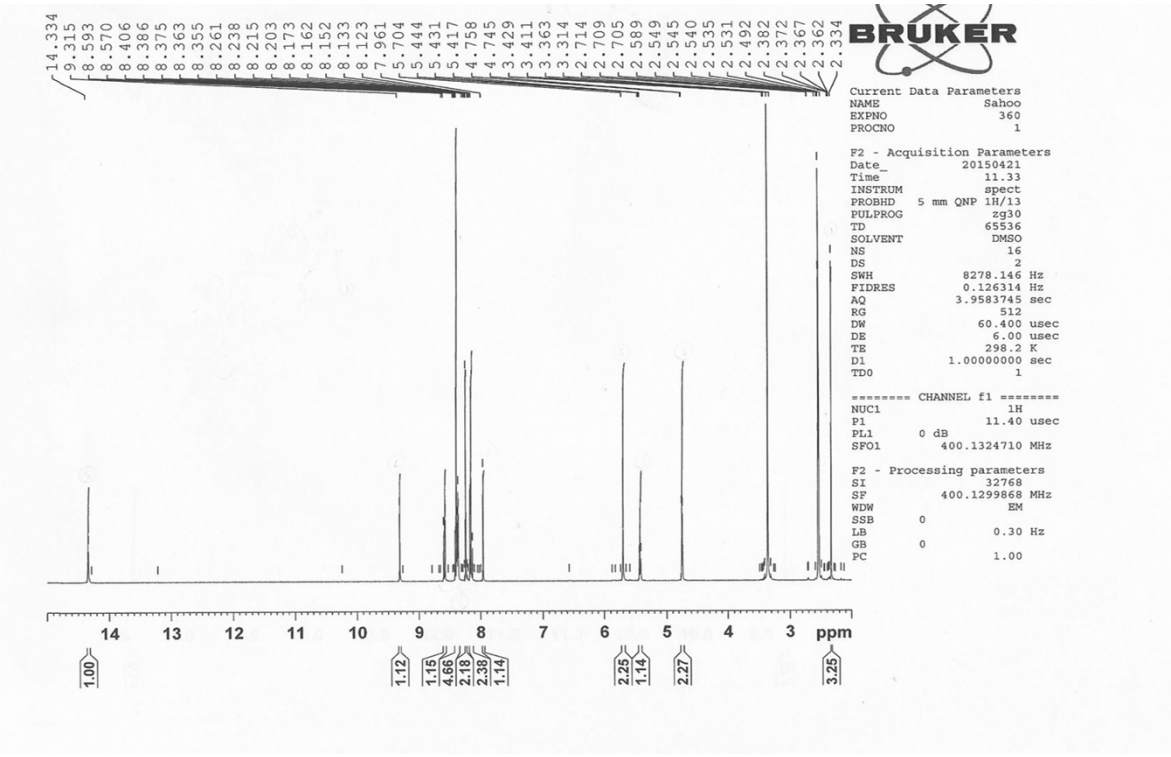

Fig. S1. ^{1}H NMR spectrum of **L** in DMSO-d_6.

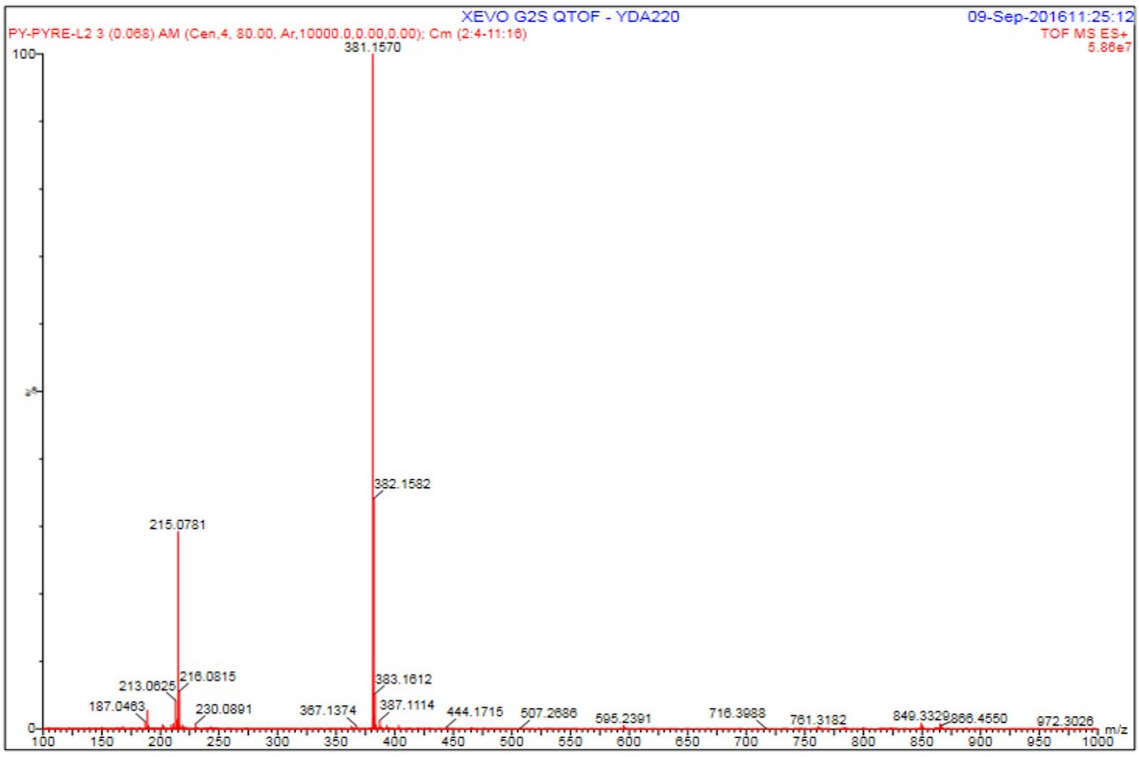

Fig. S2. HRMS spectrum of **L**.

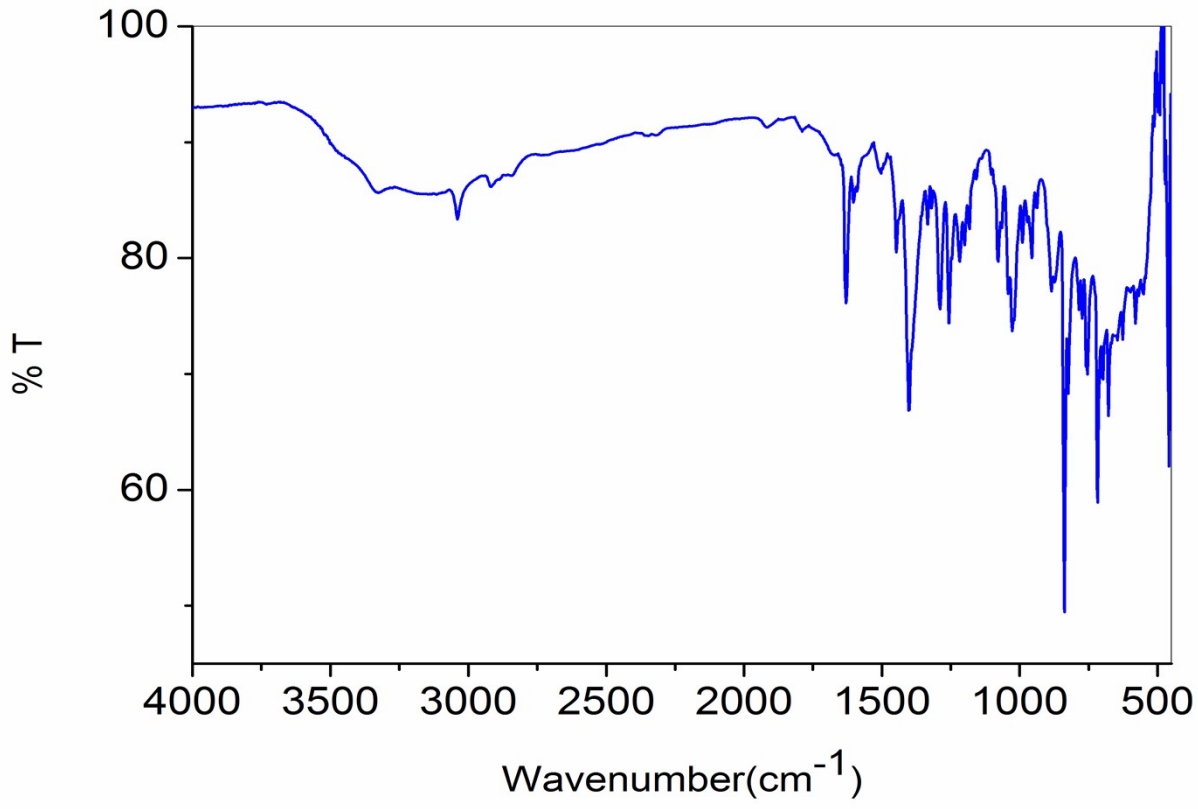

Fig. S3. ATR-FTIR spectrum of **L**.

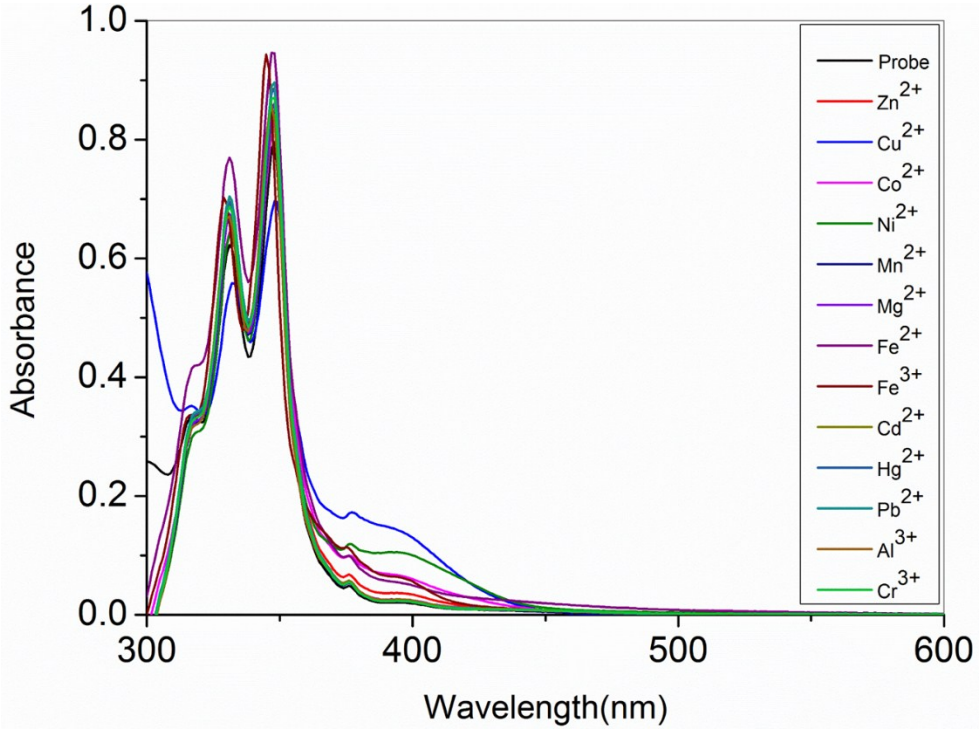

Fig. S4. UV-Visible absorbance spectra of **L** (50 µl H_2O, 1950 µl DMSO, 2.5×10^{-5}M) upon the addition of Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Al^{3+} and Cr^{3+} ions (50µL, 1×10^{-3}M, H_2O).

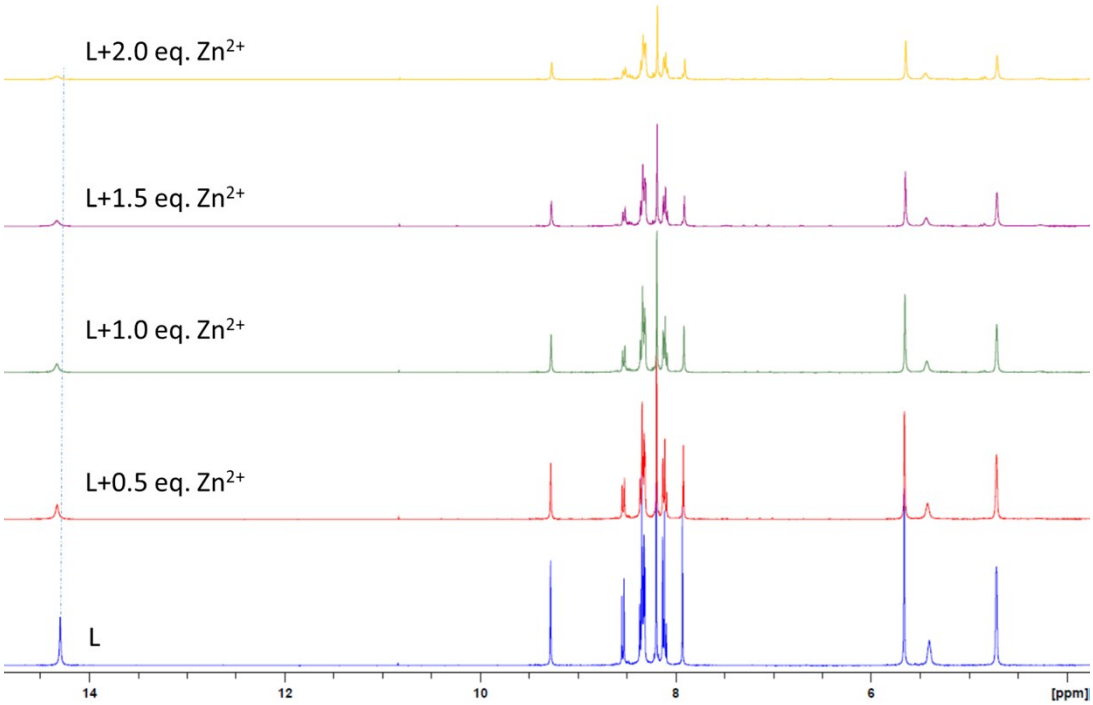

Fig. S5. ^{1}H NMR titration of **L** upon addition of Zn^{2+} ion at different equivalents in DMSO-d_6.

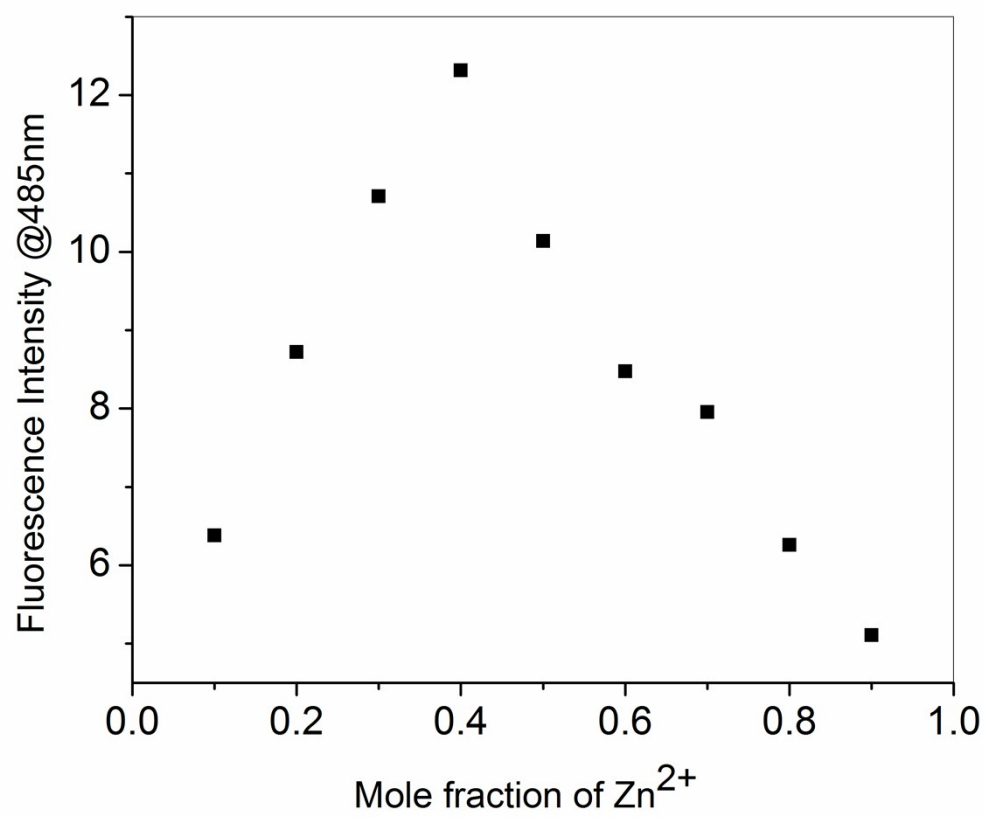

Fig. S6. The Job's plot for the complexation occurred between **L** and Zn^{2+} ion.

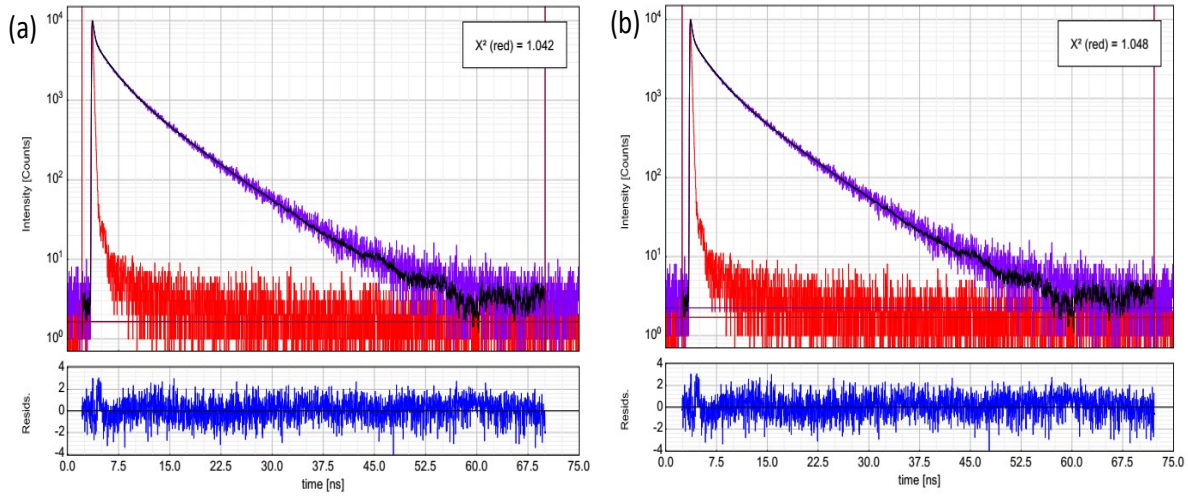

Fig. S7. Time-resolved fluorescence decay of **L** in the absence (a) and presence (b) of Zn^{2+} (λ_{exc} = 325 nm; λ_{em} = 485 nm).

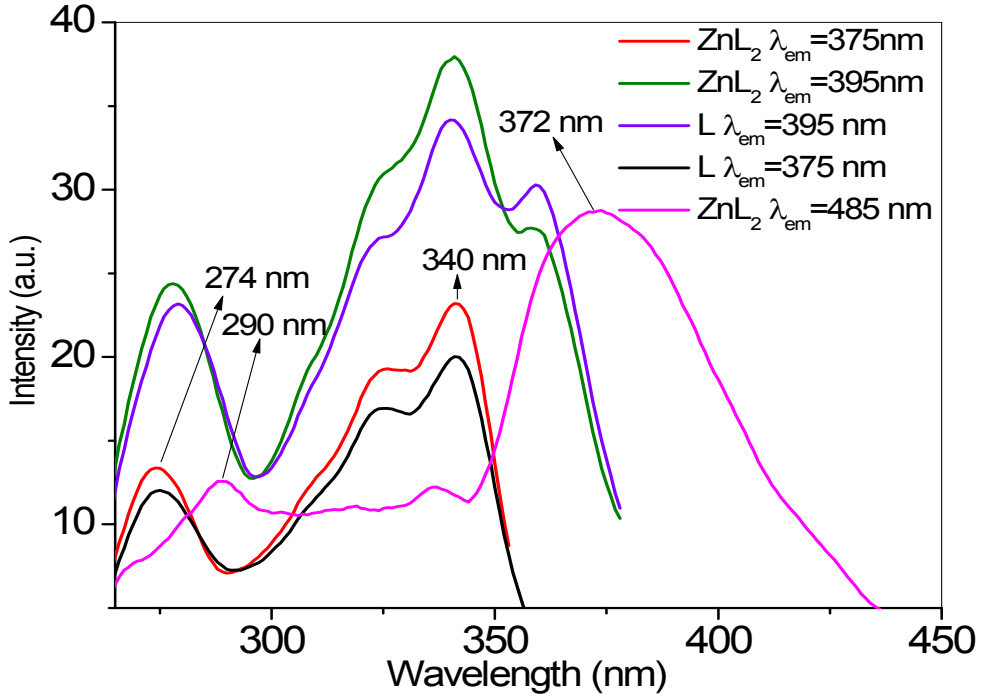

Fig. S8. Excitation spectra of the receptor **L** and its Zn**L**$_2$ complex at different λ_{em} in DMSO containing 2.5% H_2O.

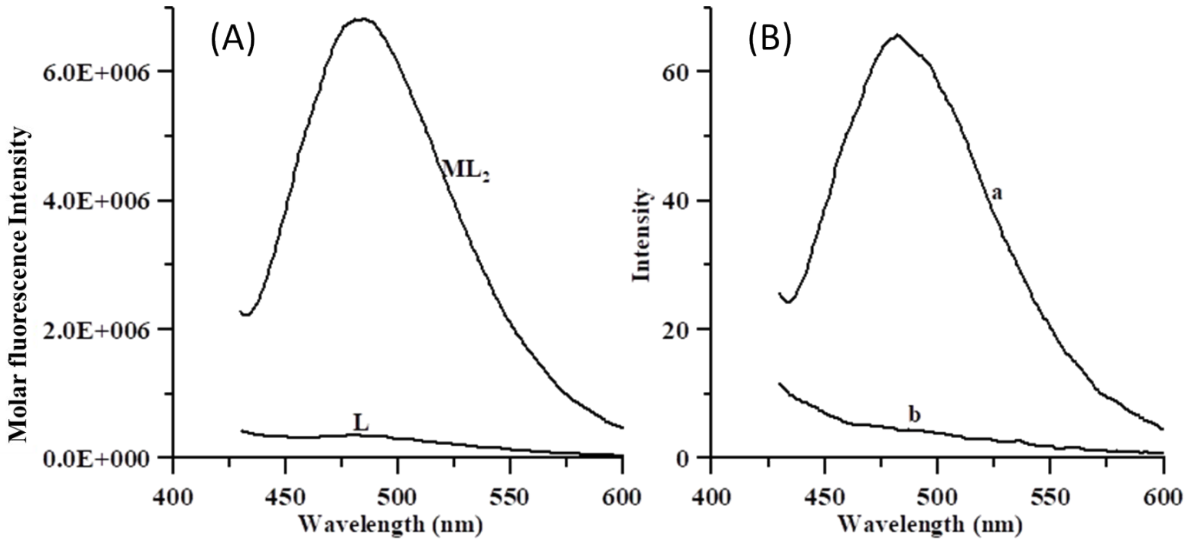

Fig. S9. (A) Calculated spectra of free receptor **L** and its Zn**L**$_2$ complex with HypSpec program, for the formation of a single complex Zn**L**$_2$ with complex formation constant log β = 10.03(1); (B) the fluorescence spectrum of **L** = 2.5x10^{-5} M in absence (b) and presence of Zn^{2+} = 3.19x10^{-5} M (a).

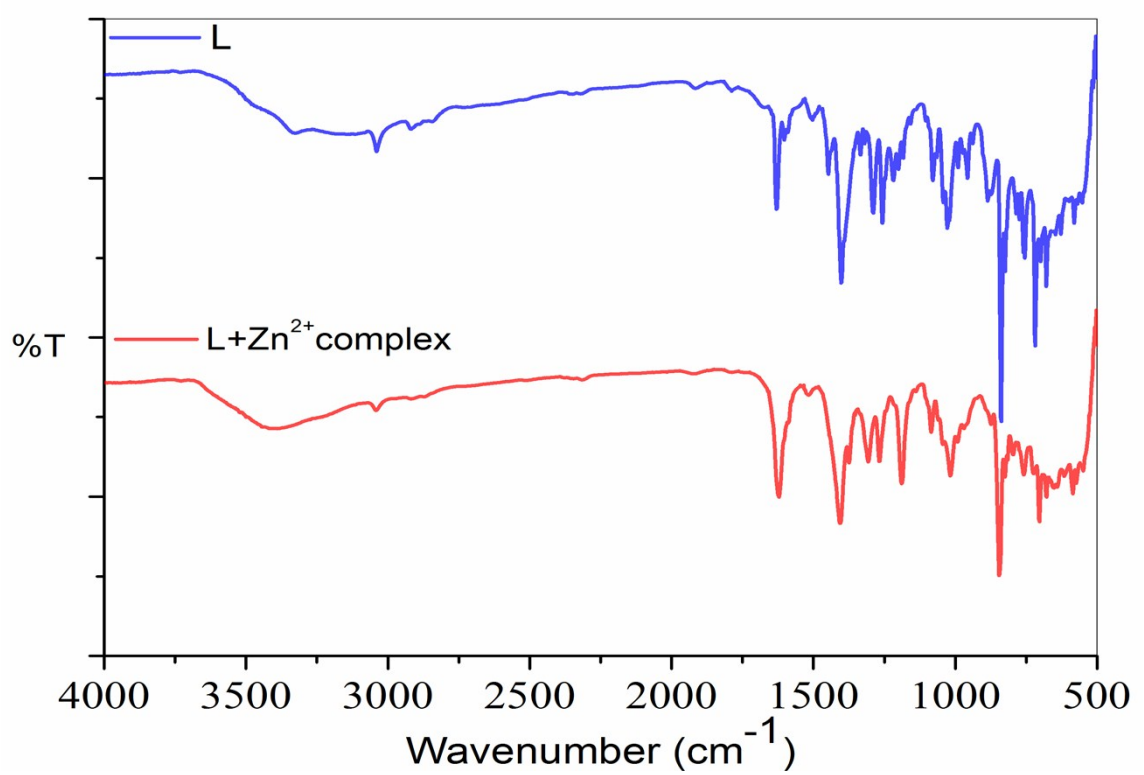

Fig. S10. ATR-FTIR spectra of **L** and its complex with Zn^{2+}.

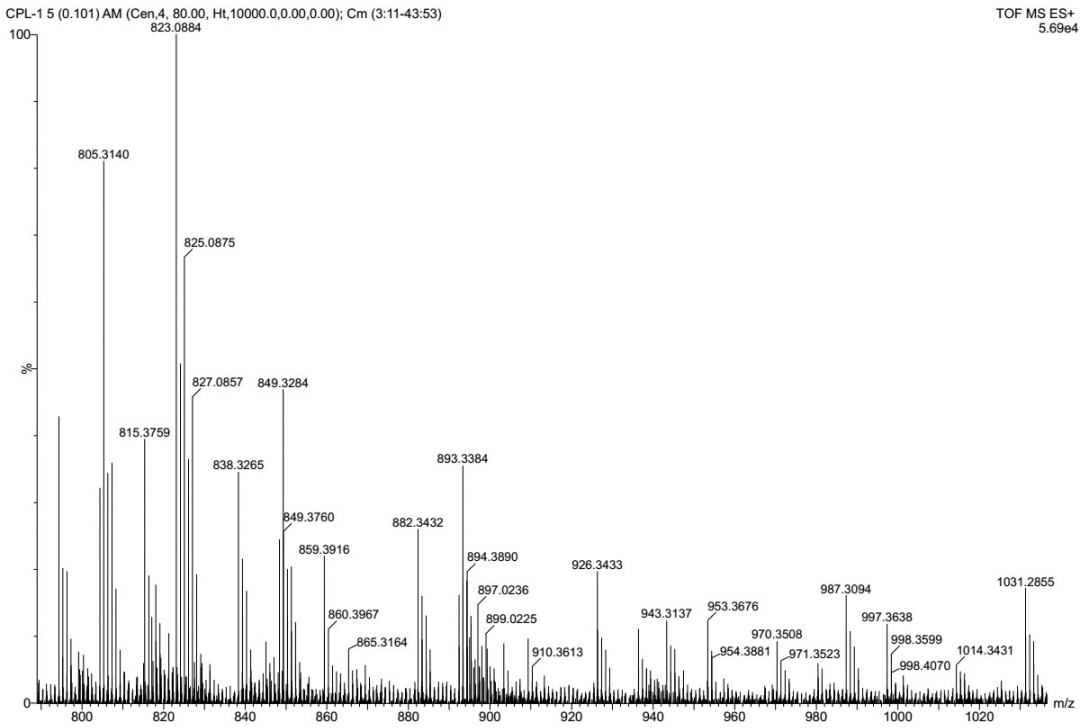

Fig. S11. HRMS spectrum of the zinc complex. The peak at m/z = 823.08 was assigned for the complex species $Zn(\mathbf{L}\text{-}H^{+})_2$.

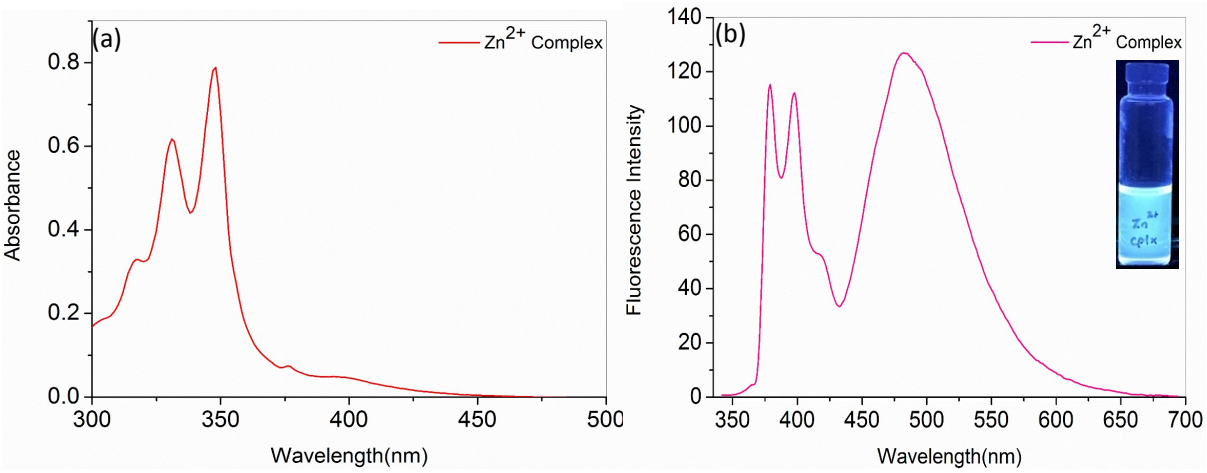

Fig. S12. (a) UV-Visible and (b) fluorescence spectra (λ_{exc} = 325 nm, slit width: 5/5 nm) of Zn(**L**-H^+)$_2$ complex (2.5×10^{-5} M) in DMSO containing 2.5% H_2O.

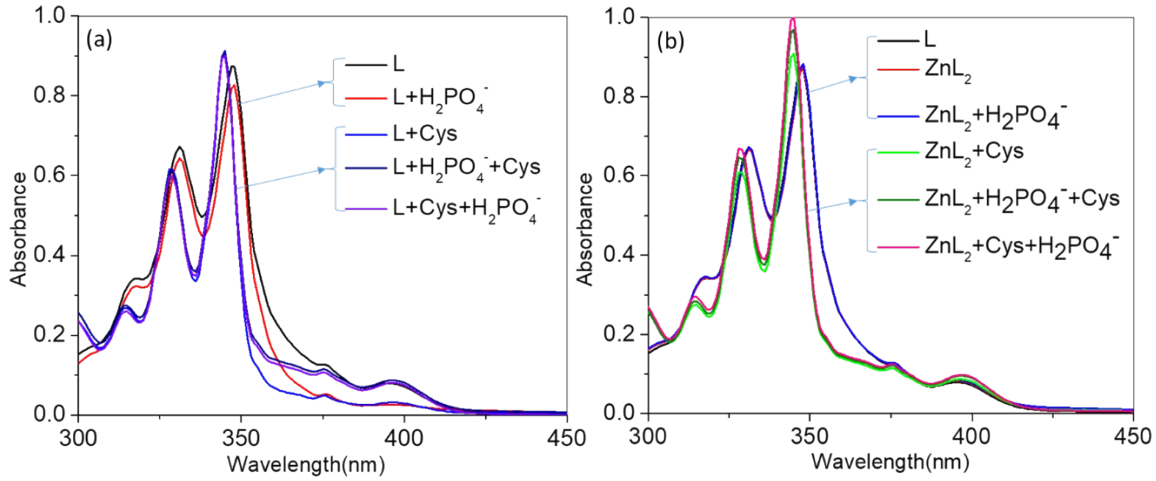

Fig. S13. UV-Visible spectra of **L** (2.5×10^{-5} M) and Zn**L**$_2$ (2.5×10^{-5} M) in the absence and presence of $H_2PO_4^-$ (50 µl, 1×10^{-3} M, H_2O) and cysteine (50 µl, 1×10^{-3} M, H_2O).

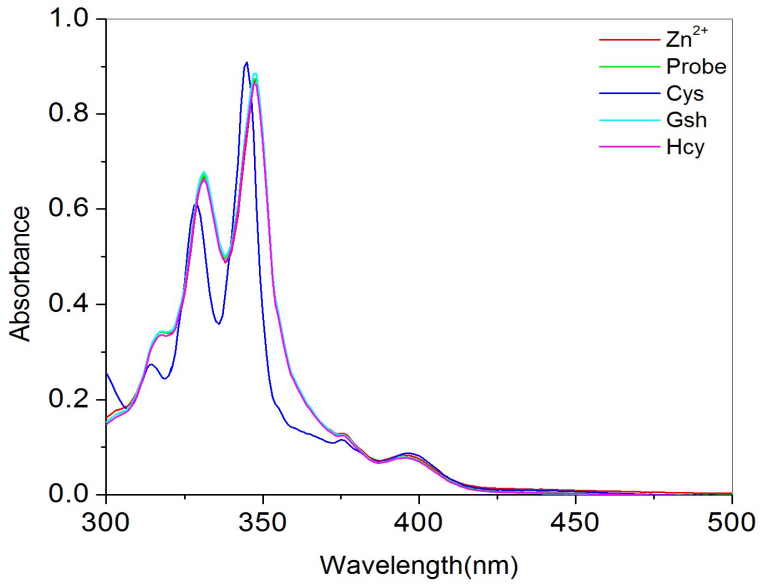

Fig. S14. UV-Visible absorbance spectra of Zn**L**$_2$ (2.5× 10^{-5} M, H_2O) with Cys, Gsh and Hcy (50 µl, 1× 10^{-3} M, H_2O).

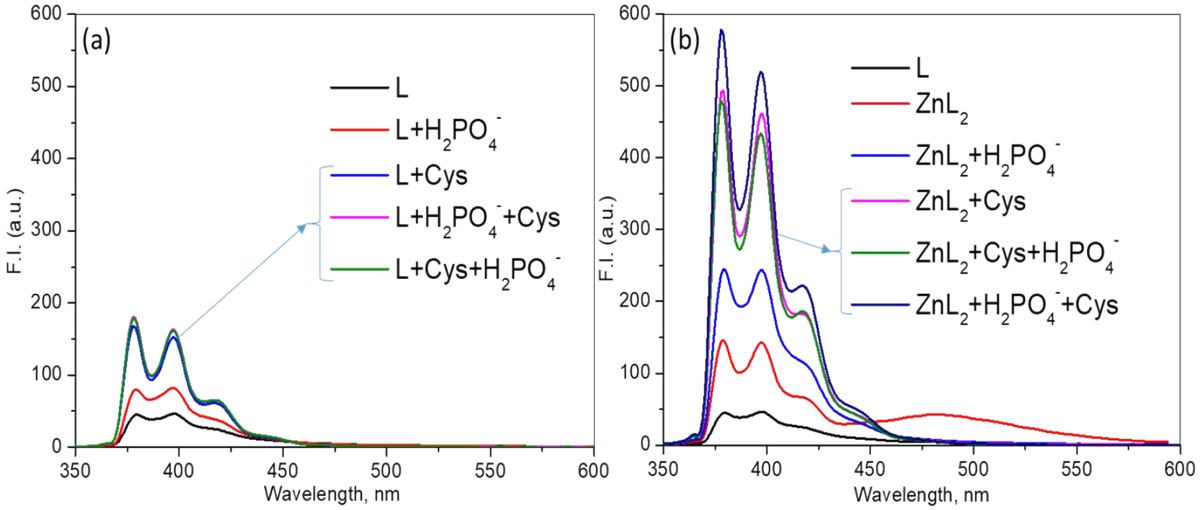

Fig. S15. Fluorescence spectra of **L** (2.5× 10^{-5} M) and Zn**L**$_2$ (2.5× 10^{-5} M) in the absence and presence of $H_2PO_4^-$ (50 µl, 1× 10^{-3} M, H_2O) and cysteine (50 µl, 1× 10^{-3} M, H_2O).

Table S1. TRPL decay constants (τ) of **L** and Zn**L**$_2$ complex.

Compounds	**τ_1(ns)**	**τ_2(ns)**	**A1%**	**A2%**	**T_{Avg}(ns)**
L	6.76	2.37	61.21	33.85	4.95
Zn**L**$_2$	6.79	2.39	60.83	34.21	4.96

Table S2. Comparison table of **L** with some reported fluorescent sensors for Zn^{2+}.

Systems	Solvent Systems	Sensing metal ion	Detection limit	Applications	Ref*
Salicylaldehyde Schiff base	MeOH:H_2O	Zn^{2+}-Turn on	1.44×10^{-7} M		1
Quinoline conjugate	MeOH:H_2O	Fe^{3+} - Colorimetry Zn^{2+}-Turn on Cu^{2+}- Turn off	10^{-6} M 10^{-5} M		2
Pyrene Schiff base	CH_3CN:H_2O	Zn^{2+}- turn on	1.38×10^{-6} M		3
Salicylhydrazide Schiff base	MeOH	Zn^{2+}- Turn on Al^{3+}-Turn on	3.33×10^{-7} M 8.31×10^{-8} M	Live cell imaging	4
Aminophenyl benzimidazole schiff base	CH_3CN:H_2O	Zn^{2+}-Turn on	4.5×10^{-9} M	-	5
Coumarin Schiff base	MeOH:H_2O	Zn^{2+}- Turn on	0.068×10^{-6}M	Live cell imaging	6
Benzimidazole Schiff base	DMSO:CH_3CN	Zn^{2+} -turn on	3×10^{-6} M	Live cell imaging	7
Pyridoxal Schiff base	EtOH:H_2O	Zn^{2+}- Turn on	μM		8
Pyrene with pyridoxal	**DMSO:H_2O**	**Zn^{2+}- Turn on**	**2.34×10^{-6} M**		**This work**

References

1. W. K. Dong, S. F. Akogun, Y. Zhang, Y. X. Sun, X. Y. Dong, *Sens. Actuators B*, 2017, **238**, 723.
2. N. Roy, S. Nath, A. Dutta, P. Mondal, P. C. Paul and T. Sanjoy Singh, *RSC Adv*., 2016, **6**, 63837.
3. C. Gao, H. Zhu, M. Zhang, T. Tan, J. Chena and H. Qiu, *Anal. Methods*, 2015, **7**, 8172.
4. Y. Fu, Y. Tu, C. Fan, C. Zheng, G. Liu and S. Pu, *New J. Chem.,* 2016, **40**, 8579.
5. S. Janakipriya, S. Tamilmanib and S. Thennarasu, *RSC Adv*., 2016, **6**, 71496.
6. C. Patra, A. K. Bhanja, A. Mahapatra, S. Mishra, K. D. Saha and C. Sinha, *RSC Adv*., 2016, **6**, 76505.
7. M. J. Kim, K. Kaur, N. Singh, D. O. Jang, *Tetrahedron*, 2012, **68**, 5429.
8. J. Wang, Y. Li, E. Duah, S. Paruchuri, D. Zhou and Y. Pang, *J. Mater. Chem*. B, 2014, **2**, 2008.

****