Supplementary Information for

A new half-condensed Schiff base platform: structures, sensing of Zn^{2+} and $H_2PO_4^-$ ions in aqueous medium

Sujaya Chakraborty[a], Somenath Lohar[a], Koushik Dhara[b], Raktim Ghosh[c], Somasri Dam[c], Ennio Zangrando[d] and Pabitra Chattopadhyay*[,a]

[a]*Department of Chemistry, The University of Burdwan, Golapbag, Purba Burdwan-713104, India.*

[b]*Department of Chemistry, Sambhu Nath College, Labpur, Birbhum 731303, West Bengal, India.*

[c]*Department of Microbiology, The University of Burdwan, Golapbag, Burdwan 713104, India.*

[d]*Dipartimento di ScienzeChimiche e Farmaceutiche, via Giorgieri, 1, 34127 Trieste, Italy.*

CONTENTS

Materials and general methods

All the analytical reagent grade solvents and the other reagent grade chemicals consumed in this work were procured from commercial sources and used as received. Here, throughout the experiments, Milli-Q 18 Ω water was employed. 2,6-Diformyl-p-cresol was synthesized following the literature procedure[1]. *2-hydroxy-5-methyl-3-[(2-phenylamino-phenylimino)-methyl]-benzaldehyde* was prepared by the method mentioned in the manuscript. Elemental analyses (C, H and N) were carried out on a Perkin Elmer 2400 CHN elemental analyzer.The electrospray ionization (ESI) mass spectra were measured using the Waters (Xevo G2 Q-TOF) mass spectrometer. Systronics digital pH meter (model 335) was used for pH study and the adjustment of pH was done using either 50 mM HCl or NaOH solution. Absorption spectra were measured using a Shimadzu-2450 UV-vis spectrophotometer. Fluorescence measurements were performed with a Hitachi-4500 spectrofluorimeter (All emission spectra were collected with the emission slits set at 5 nm.).

The selectivity study was carried out by Li^{+}, Na^{+}, K^{+}, and Cs^{+}, Mg^{2+}, Ba^{2+}, Ca^{2+}, Sr^{2+}, Fe^{2+}, Fe^{3+} Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+}, and Hg^{2+} metal ion of chloride, nitrate, sulphate and acetate salts and the sodium/potassium salts of hypochlorite, chlorate, thiocyanate, cyanide, azide, bicarbonate, nitrate, arsenite, arsenate, monohydrogen phosphate, phosphate, sulphate, sulphide and tetrabutylammonium salts of halides (F^{-}, Cl^{-}, Br^{-}, I^{-}), acetate, dihydrogen phosphate etc. in 10 mM HEPES buffer, pH 7.4, water/DMSO (v/v 3:1) solution with an HL′ concentration of 10 μM solution. In the study of selectivity, the amount of the cations and anions weretaken as 10 equivalent greater than that of the probe used.

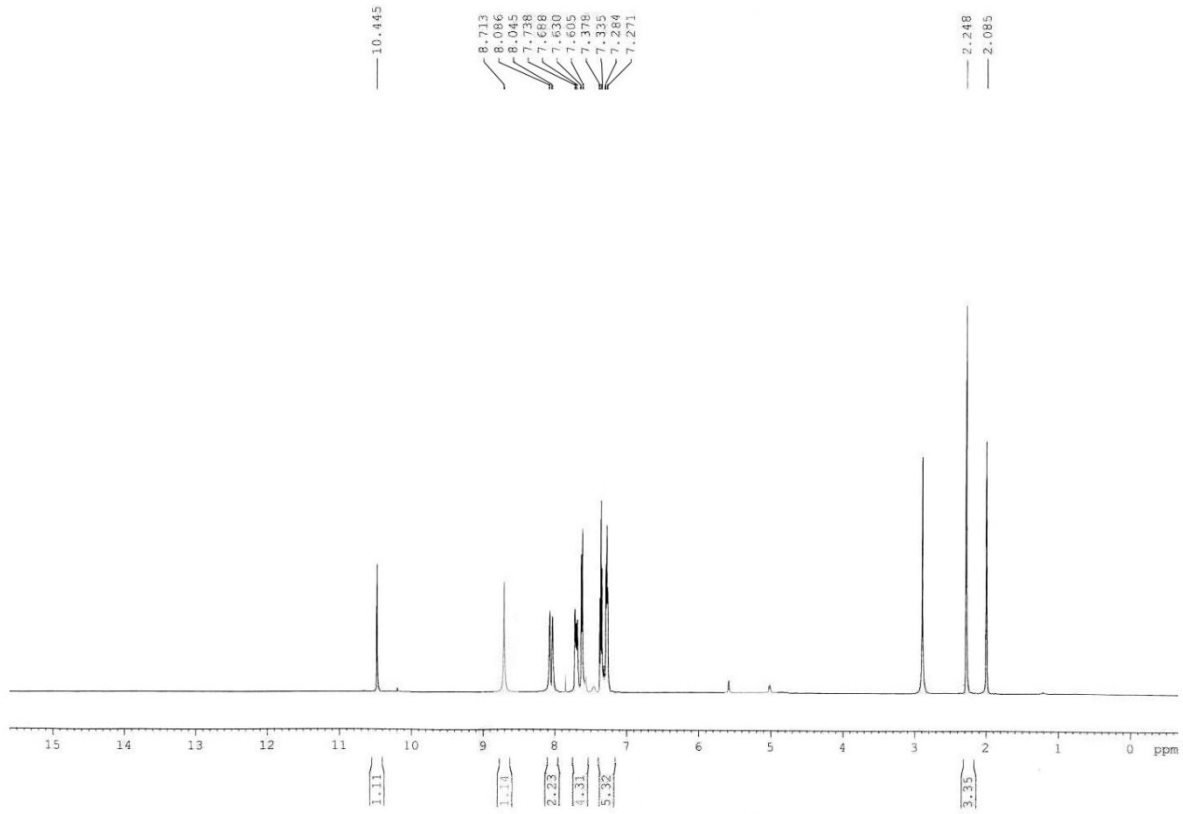


Fig. S1. ^{1}H NMR spectrum of **HL′** (i.e. generated **HL** in solution) in d_6-acetone

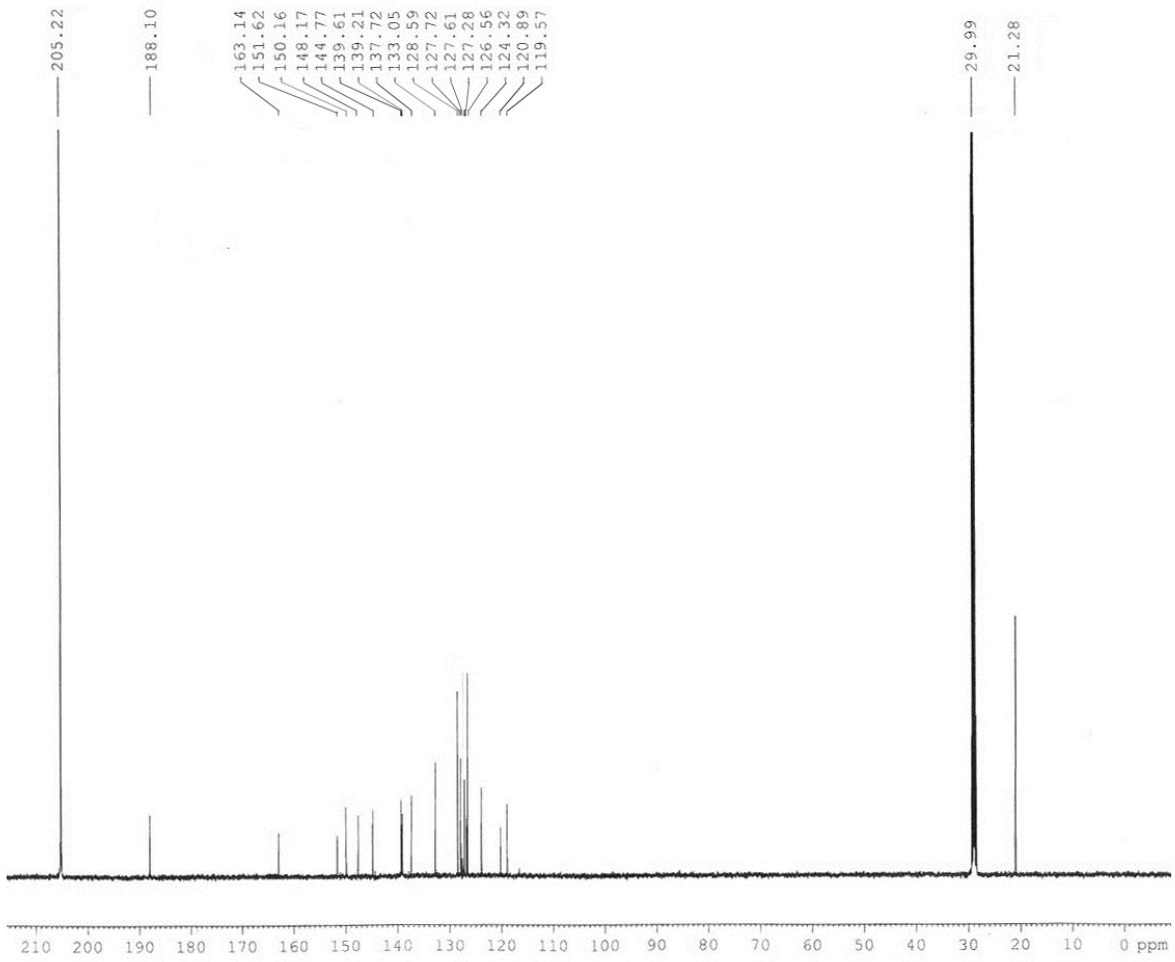


Fig. S2. ^{13}C NMR spectrum of **HL′** (i.e. generated **HL** in solution) in d_6-acetone

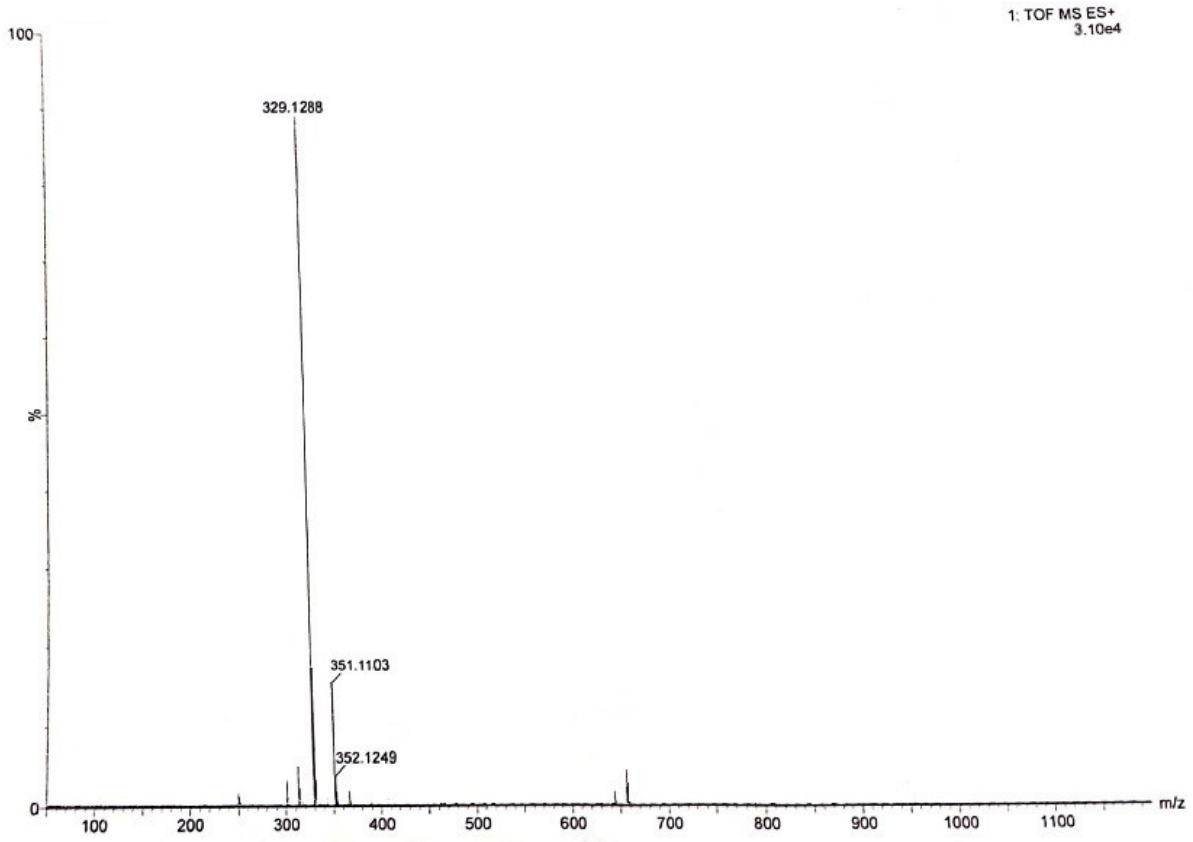


Fig. S3. HRMS spectrum of **HL′** (i.e. generated **HL** in solution) in MeOH [found m/z, 329.1288 and m/z, 351.1103, calculated for [M+H$^+$] (m/z, 329.1285) and [M+Na$^+$] (m/z 351.11040 respectively, where M is $C_{21}H_{16}N_2O_2$ (HL)].

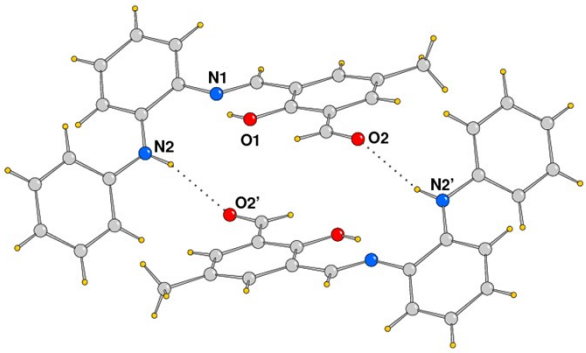
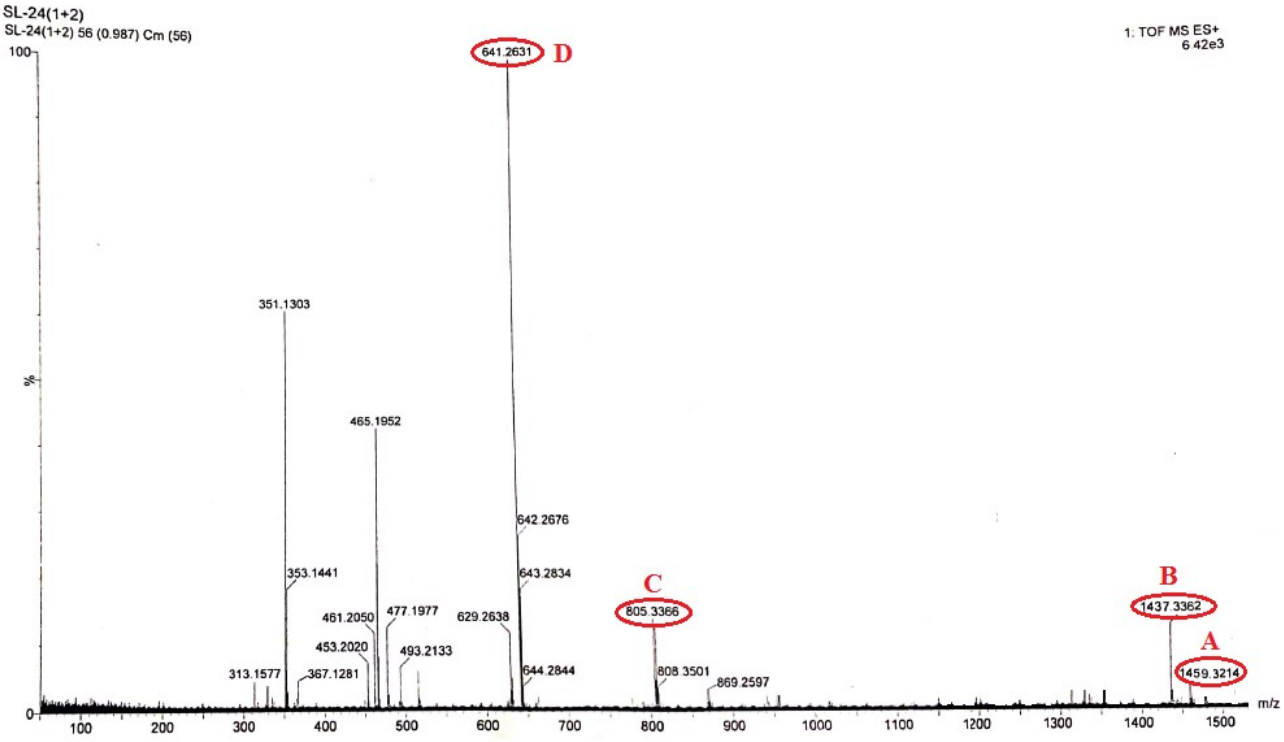


Fig. S4. Formation of centrosymmetric dimers in the crystal packing of HL′ through weak NH…O hydrogen bonds.



A: $[Zn_2L_4+Na^+]$, (Exact Mass: 1459.3009); **B:** $[Zn_2L_4+H^+]$, (Exact Mass: 1437.3190);

C: $\{[ZnL_2(MeOH)_2]+Na^+\}$, (Exact Mass: 805.1980);

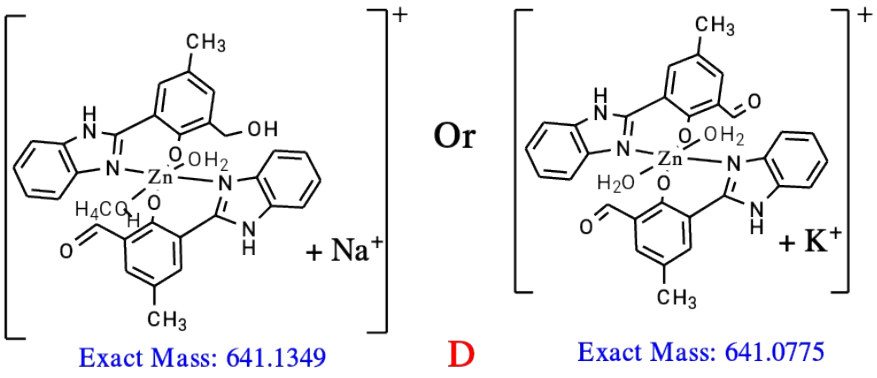


Fig.S5. HRMS of the Zn^{2+} complex (Zn_2L_4) in methanol.

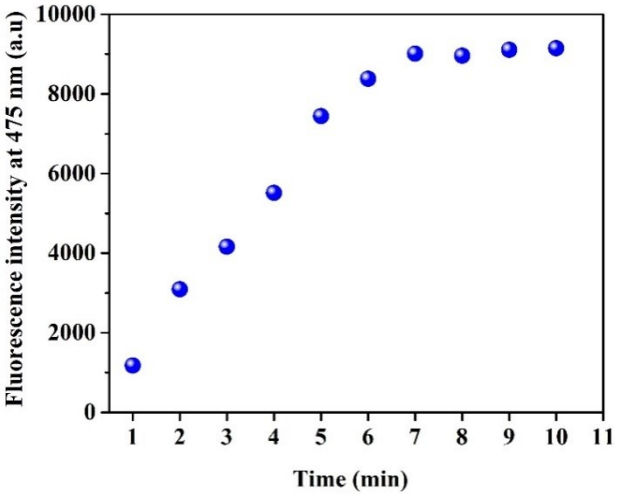


Fig. S6. Time dependent fluorescence study of **HL′** (i.e. generated **HL** in solution) (10 μM) in presence of Zn^{2+} ion (100 μM) in reaction buffer [10 mM HEPES, water/DMSO v/v 3:1, pH 7.4] at 25 °C (λ_{ex}: 355 nm).

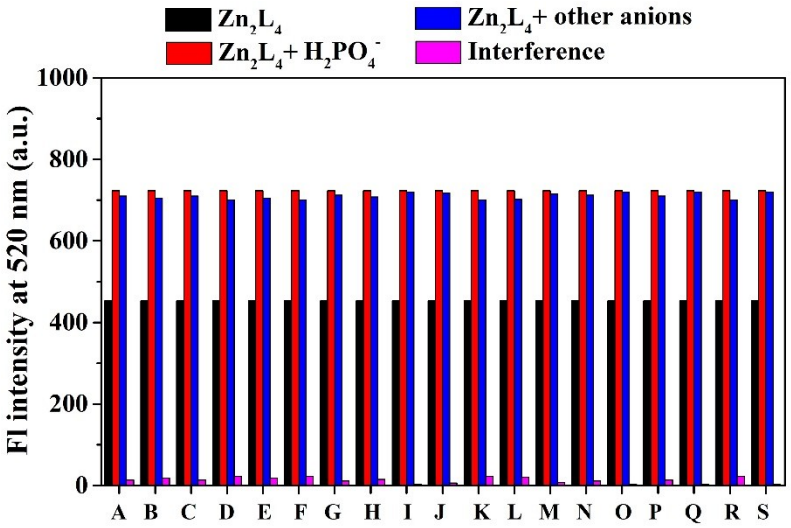


Fig. S7. Relative fluorescence study of the mixture of Zn_2L_4complex (10 μM) in presence of $H_2PO_4^-$ ion (100 μM) and other anions (A) F^- , (B) Cl^- , (C) Br^- , (D) CN^- , (E) I^- , (F) SCN^- ,(G) NO_3^- , (H) ClO_3^- , (I) ClO_4^- , (J) $H_2AsO_4^-$, (K) $HSO4^-$, (L) HS^- , (M) $HAsO_4^{2-}$, (N) S^{2-} , (O) $S_2O_3^{2-}$, (P) SO_4^{2-} , (Q) HPO_4^{2-} , (R) PO_4^{3-} and (S) $P_2O_7^{4-}$ in reaction buffer at 25 °C (ex: 355 nm).

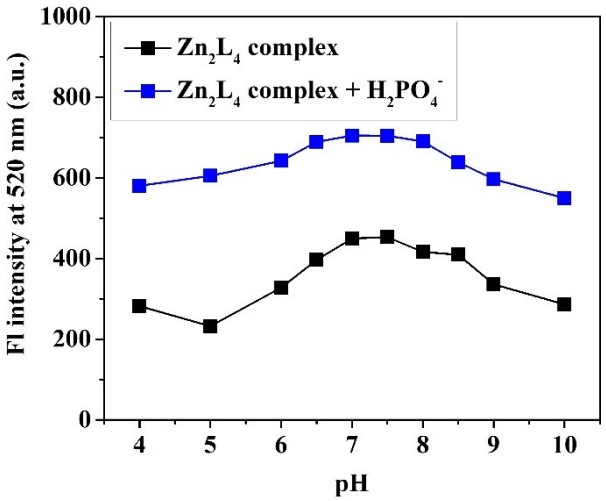


Fig. S8. pH study of Zn_2L_4 complex (10 μM) in absence and presence of $H_2PO_4^-$ ion(100 μM) in reaction buffer of pH 4 to 10 at 25 °C (λ_{ex}: 355 nm).

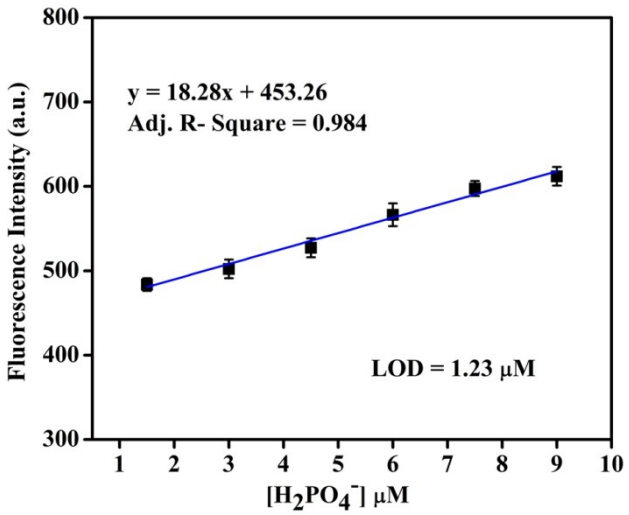


Fig. S9. Calibration curve in the nanomolar range, with error bars to calculate the LOD of $H_2PO_4^-$ ion in reaction buffer at 25 °C (Fluorescence intensity was measured at 520 nm) (λ_{ex}: 355 nm).

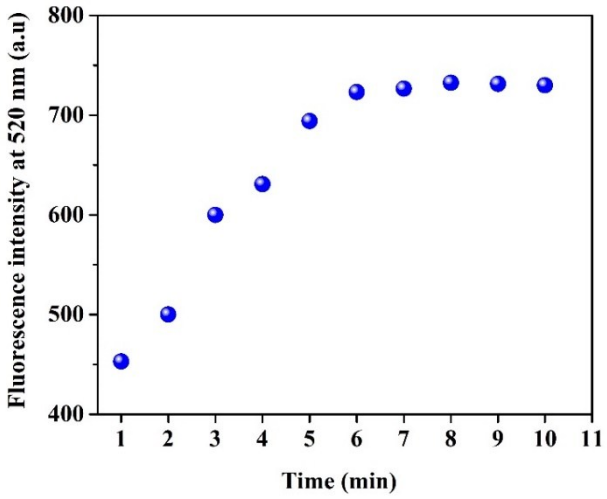


Fig. S10. Time dependent fluorescence study of **Zn_2L_4** complex (10 μM) in presence of $H_2PO_4^-$ ion (100 μM) in reaction buffer at 25 °C (λ_{ex}: 355 nm).

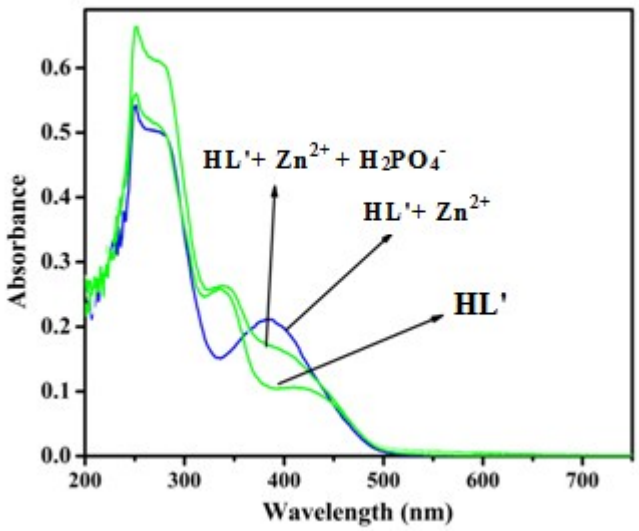


Fig. S11. UV-vis spectra of HL′, HL′+ Zn^{2+} ion, and HL′+ Zn^{2+} + $H_2PO_4^-$ ion in reaction buffer at 25 °C, (i.e. here also HL′ as HL in solution state)

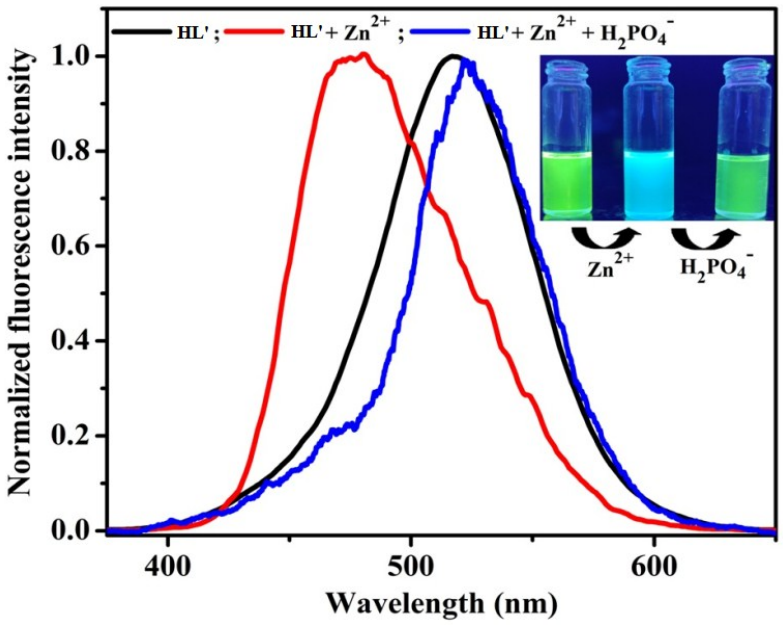


Fig. S12. Fluorescence spectra of HL′, HL′+ Zn^{2+} ion, and HL′+ Zn^{2+} + $H_2PO_4^-$ ion in reaction buffer at 25 °C (λ_{ex}: 355 nm) (here also HL′as HL in solution state)

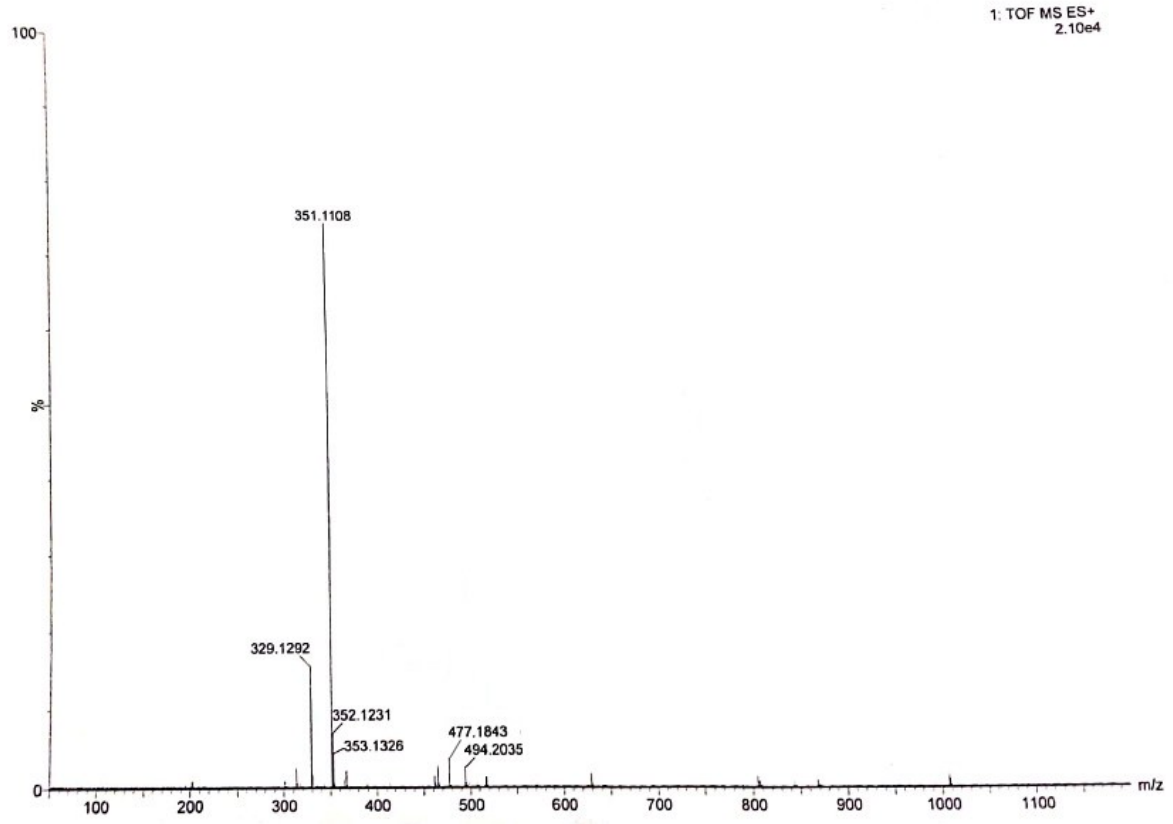


Fig. S13. HRMS data of the reaction between $\mathbf{Zn_2L_4}$ complex and $H_2PO_4^-$ ion, found at m/z, 329.1292 and at m/z, 351.1108, calculated for [M+H$^+$] (m/z, 329.1285) and [M+Na$^+$] (m/z, 351.1104) respectively where M was $C_{21}H_{16}N_2O_2$ (HL) in MeOH. Mass experiment was carried out with the filtrate obtained after the mixing of Zn(II) complex and $H_2PO_4^-$ ion in the reaction buffer for 20 min.

Table S1 Crystallographic data and details of refinements for HL′ and Zn(II) complex.

Empirical Formula	$C_{21}H_{18}N_2O_2$	$C_{85}H_{61.50}N_{8.50}O_{10}Zn_2$
Formula Weight	330.37	1492.66
Crystal system	monoclinic	monoclinic
Space group	***P 2$_1$/c***	***C 2/c***
a (Å)	16.0146(5)	21.562(5)
b (Å)	7.3894(3)	21.886(5)
c (Å)	14.6908(5)	15.803(3)
α	90.00°	90.00°
®	101.708(2)°	97.202(5)°
γ	90.00°	90.00°
Volume (Å^3)	1702.31(11)	7399(3)
Z	4	4
$\rangle_{calc}$ (g/cm^3); μ (mm^{-1})	1.289; 0.084	1.340; 0.715
\ range (deg)	3.248- 26.702°	2.81- 27.47°
Reflections collected	26400	60557
Reflections independent	3591	9249
goodness of fit values	0.938	1.058
Final R indices [$I > 2\sigma(I)$]	R = 0.0467 , wR2=0.1228	R = 0.0503, wR2= 0.1448

Table S2 Selected bond distances (Å) and bond angles (°) for HL′.

Bond length (Å)			
O2 – C7	1.345(2)	N1- C9	1.279(2)
O1 - C1	1.201 (2)	N1 - C10	1.416(2)
O2 - H1	0.8200	N2 – C15	1.391(2)
C10 - C15	1.393(3)	C2 - C3	1.393(2)
N2 - H13	0.8600	C15 – C14	1.389(3)
N2 – C16	1.395(2)		
Bond angles (º)			
C9- N1 –C10	121.26(16)	N2- C15- C10	118.74(16)
C14- C15- N2	122.38(18)	C4- C3- C2	122.67(18)
C15 -N2 -C16	126.39(16)	C7 –C6- C9	121.14(16)
N1- C9- C6	122.30(16)	C3- C4- C5	116.91(17)
N1- C9- H8	118.8	C11 –C10- N1	122.38(18)
C16- C17 -C18	120.1(2)	C19 –C18- C17	120.6(2)
C14- C15- N2	122.81(21)		

Table S3 Selected bond distances (Å) and bond angles (°) for Zn(II) complex.

Bond length (Å)			
Zn1– O2	2.0382(16)	O4 – Zn1	2.1601(18)
Zn1– O1	2.0440 (17)	N1 – C8	1.321(3)
Zn1– N3	2.0612(19)	N2 – C16	1.389(3)
Zn1– O4	2.1602(19)	C2 - C3	1.393(4)
N2 – C9	1.433(3)	N5 – C51	1.023(10)
N2 – C16	1.389(3)		
Bond angles (º)			
O2- Zn1 - O1	96.87(7)	C28- N3- Zn1	125.19(15)
O2- Zn1 – N3	155.51(7)	C35- N3- Zn1	125.53(15)
O2- Zn1 – O4	87.09(7)	C21- O2- Zn1	126.39(14)
N3- Zn1- O4	87.95(7)	Zn1- O2- Zn1	102.54(7)
N1- Zn1- O2	101.18(6)	C29 –C34- C33	118.7(3)
C15- N1 –Zn1	130.41(15)	C37 –C36- C35	117.0(2)
C8- N1 –Zn1	121.36(15)		

Reference:

1. S. Lohar, S. Pal, B. Sen, M. Mukherjee, S. Banerjee and P. Chattopadhyay, *Anal. Chem*., 2014, **86**, 11357.