Supporting Information

A cationic tetrahedral Zn(II) cluster based on a new salicylamide imine multidentate ligand: Synthesis, structure, stability and fluorescence sensing study

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Table S1. Crystallographic data and details of refinements for **Zn_4L_3**.

CCDC number	1821832
Empirical formula	$Zn_{16}C_{228}H_{254}N_{28}O_{81}$
Formula weight	5728.82
Temperature	293(2)
Crystal system, space group	Cubic, Pa-3
Unit cell dimensions	*a = b = c = 22.59190(10)* Å
	$\alpha = \beta = \gamma = 90^\circ$
Volume, Z	11530.7715), 2
Absorption coefficient	2.615 mm^{-1}
F(000)	5892
2θ range for data collection	4.795 to 69.753°
Limiting indices	-27 ≤ h ≤ 10; -9 ≤ k ≤ 27; -14≤ l ≤ 27
R_{int}	0.0255
Reflections collected / unique	10234 / 3636
Completeness	99.6 %
Absorption correction	Multi-Scan
Data/restraints /parameters	3636/4/289
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R_1 = 0.0325, wR_2 =0.0846
R indices (all data)	R_1 = 0.0408, wR_2 =0.0915
Largest diff. peak and hole	0.289 and -0.375 e· Å^{-3}

Table S2. Selected bond lengths (Å) and angles (°) for **Zn_4L_3**.

Zn1–N1	2.019(2) 9	Zn1–O4	1.9305(17)	Zn1–O2	1.9975(16)	Zn1–O6	2.0318(9)	Zn1–O5	2.4426(18)
Zn2–O2	1.9982(17)	Zn2–O1	2.1514(18)						
O4–Zn1–O2	141.00(8)	O4–Zn1–N1	114.14(8)	O2–Zn1–N1	93.60(8)	O4–Zn1–O6	91.77(6)		
O2–Zn1–O6	91.51(9)	N1–Zn1–O6	128.28(8)	O4–Zn1–O5	71.85(7)	O2–Zn1–O5	86.05(7)		
N1–Zn1–O5	82.65(8)	O6–Zn1–O5	149.06(6)	O2–Zn2–O2	96.22(7)	O2–Zn2–O1	94.87(8)		
O2–Zn2–O1	167.89(7)	O2–Zn2–O1	77.72(7)	O2–Zn2–O1	77.72(7)	O2–Zn2–O1	94.87(8)		
O2–Zn2–O1	167.88(7)	O1–Zn2–O1	92.23(7)	O2–Zn2–O1	167.89(7)	O2–Zn2–O1	77.72(7)		
O2–Zn2–O1	94.87(8)	O1–Zn2–O1	92.23(7)	O1–Zn2–O1	92.23(8)				

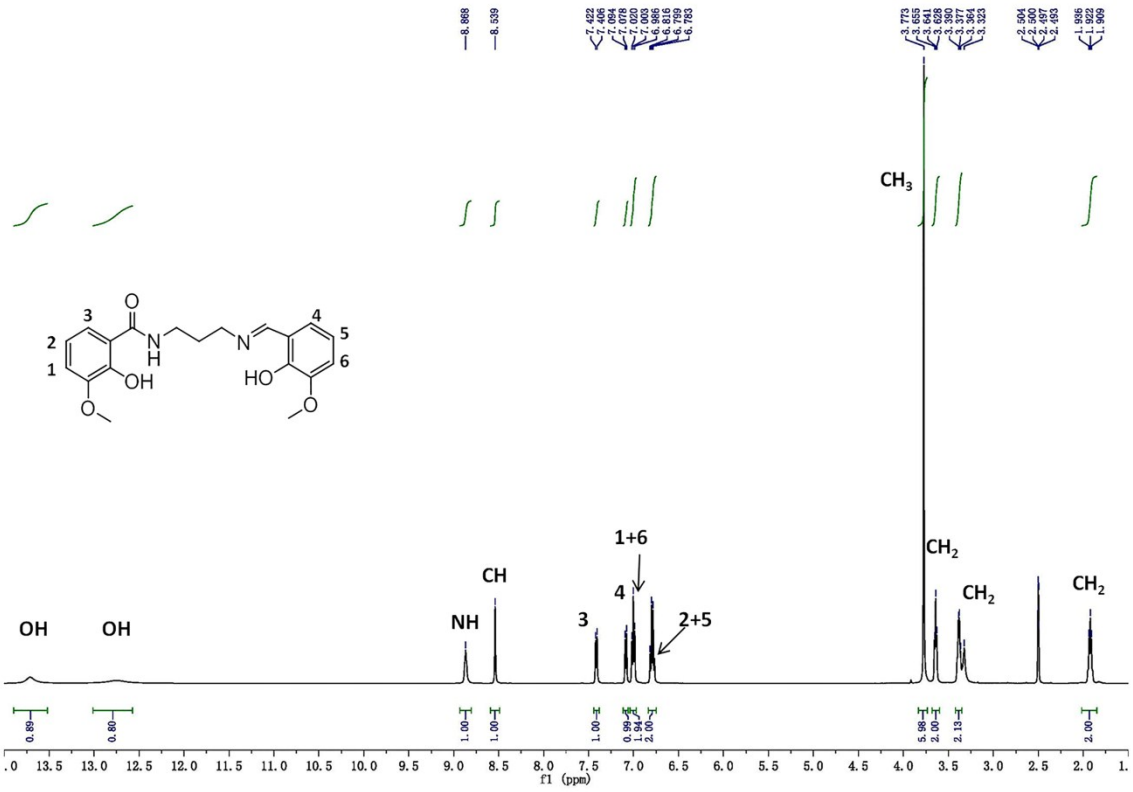

Figure S1. The ^{1}H NMR spectra of H_2L and its assignment in d_6-DMSO solution.

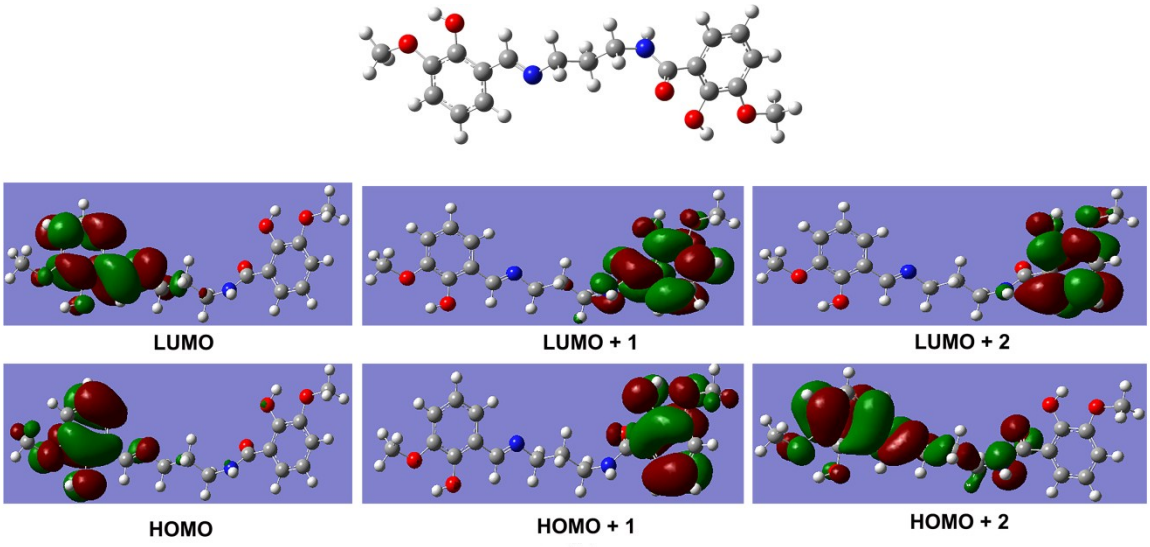

Figure S2. Optimized molecular geometry of H_2L and its' contour plots of the frontier orbitals.

The cartesian coordinate of the optimized structure of H_2L are as follows:

B3LYP/6-31G(d, p) in gas phase, E = -1222 a.u., Charge = 0, Multiplicity = 1

C	1.12983	-2.17341	-0.41042
H	0.86017	-3.07149	0.16147
H	1.34962	-2.47753	-1.43772
C	-0.0281	-1.15993	-0.39368
H	-0.20873	-0.81232	0.6333
H	0.24643	-0.28158	-0.98792
C	-1.32815	-1.76213	-0.95509
H	-1.6253	-2.64919	-0.36477
H	-1.15022	-2.09535	-1.98664
N	-2.3848	-0.74617	-0.99163
N	2.37464	-1.62345	0.12906
H	2.42857	-1.42293	1.11723
C	3.40932	-1.21504	-0.68181
C	-3.48495	-0.96171	-0.35836
H	-3.66333	-1.88717	0.20156
O	3.36569	-1.31624	-1.92659
C	-4.57681	0.01979	-0.34597
C	-5.75691	-0.25335	0.35767
C	-4.47313	1.24989	-1.03153
C	-6.81008	0.6814	0.37595
C	-5.51564	2.1695	-1.01001
H	-3.55481	1.44645	-1.57148
C	-6.70021	1.89055	-0.30156
H	-5.42333	3.11066	-1.54108
H	-7.50898	2.61164	-0.28944
C	4.60536	-0.69246	0.06001
C	5.20645	-1.46913	1.07166
C	5.17866	0.53999	-0.26901
C	6.3577	-1.03368	1.7267
H	4.77467	-2.43396	1.31587
C	6.33957	0.97733	0.40192
C	6.93508	0.20147	1.39147
H	6.81649	-1.64993	2.49204
H	7.82929	0.54017	1.90098
O	4.5979	1.35885	-1.21337
H	5.14853	2.16404	-1.31832
O	-5.90156	-1.44775	1.04601
H	-6.78569	-1.46094	1.47047
O	-7.91211	0.24858	1.12512
O	6.77856	2.23192	-0.03485
C	7.97883	2.7976	0.55127
H	8.12111	3.75568	0.05298
H	7.85216	2.95366	1.62869
H	8.84491	2.15119	0.36972
C	-9.06945	1.1168	1.22625
H	-9.50377	1.30646	0.23807
H	-9.78408	0.57821	1.8475

H	-8.80444	2.06776	1.7022

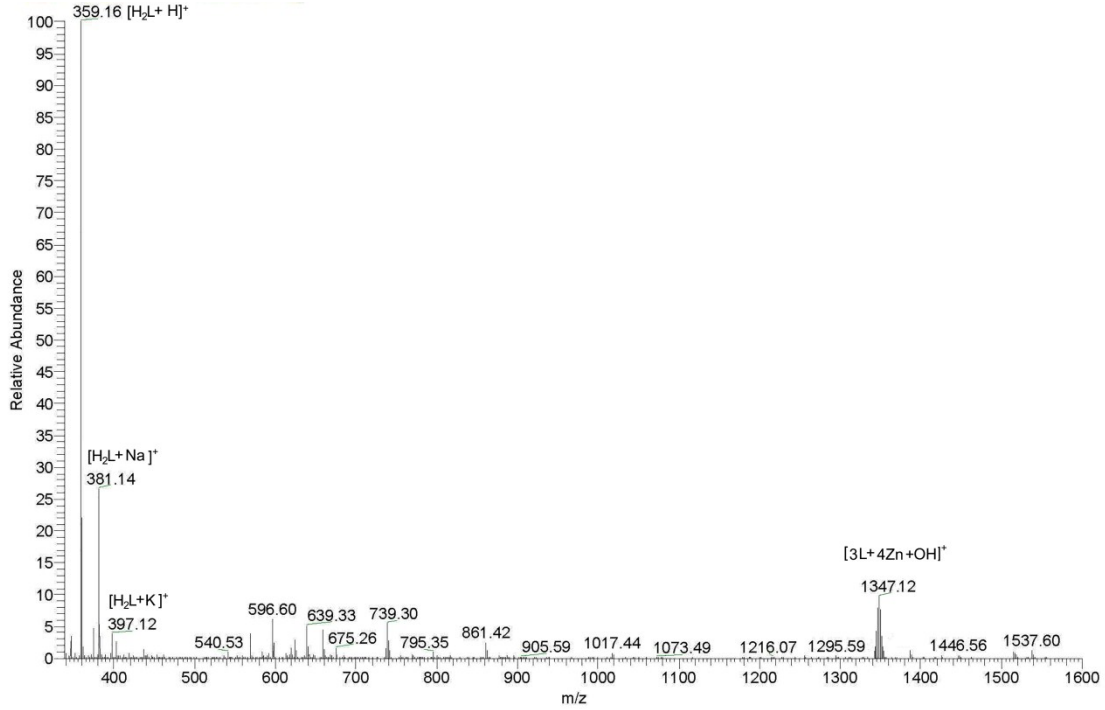

Figure S3. The high resolution ESI mass spectrum of Zn_4L_3 in DMSO + H_2O (V : V =9 : 1) solution.

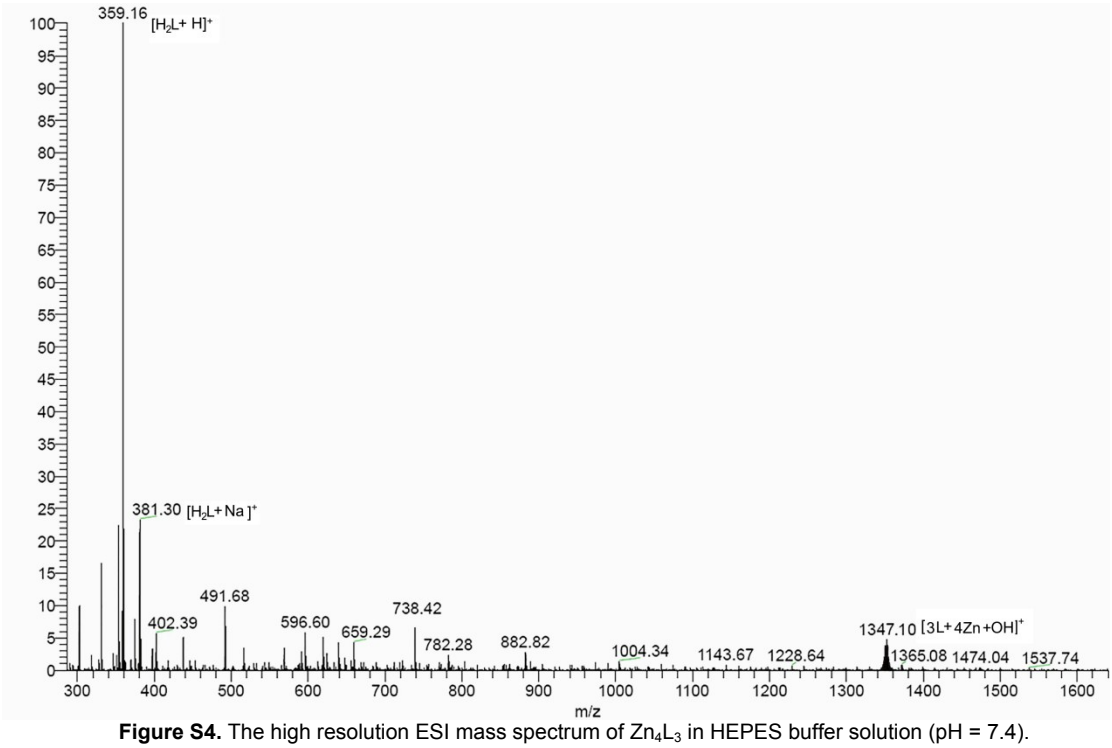

Figure S4. The high resolution ESI mass spectrum of Zn_4L_3 in HEPES buffer solution (pH = 7.4).

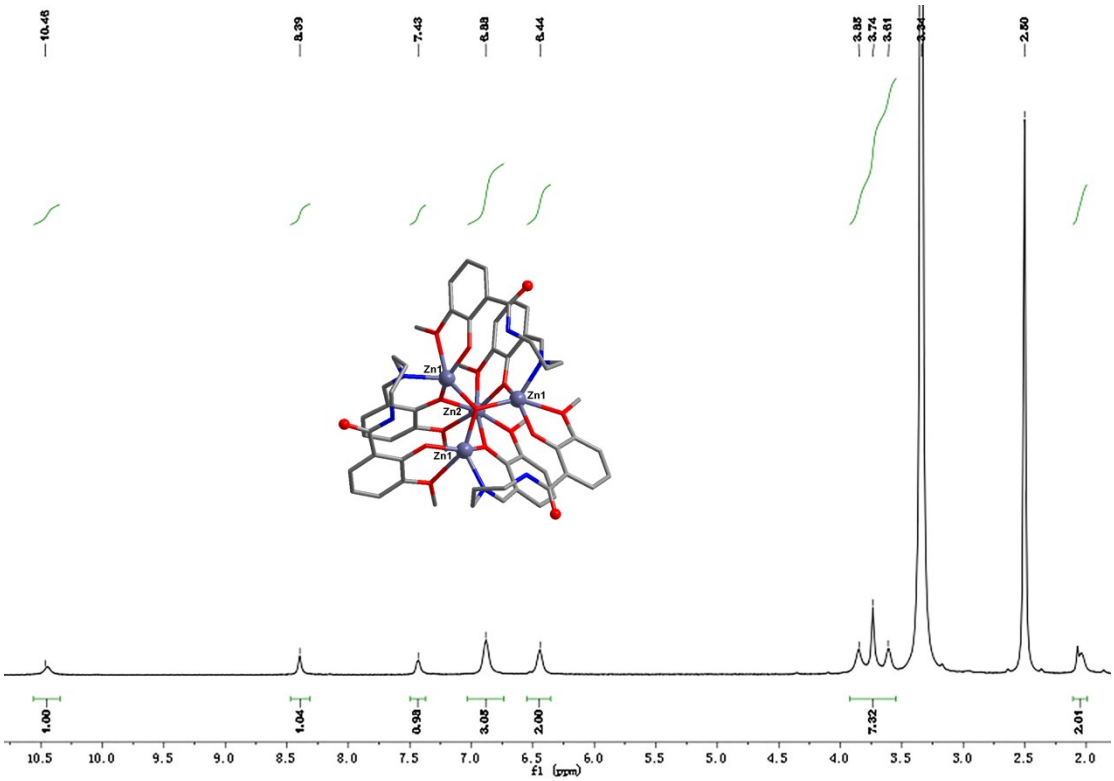

Figure S5 The ^{1}H NMR spectra of Zn_4L_3 in d_6-DMSO + D_2O solution.

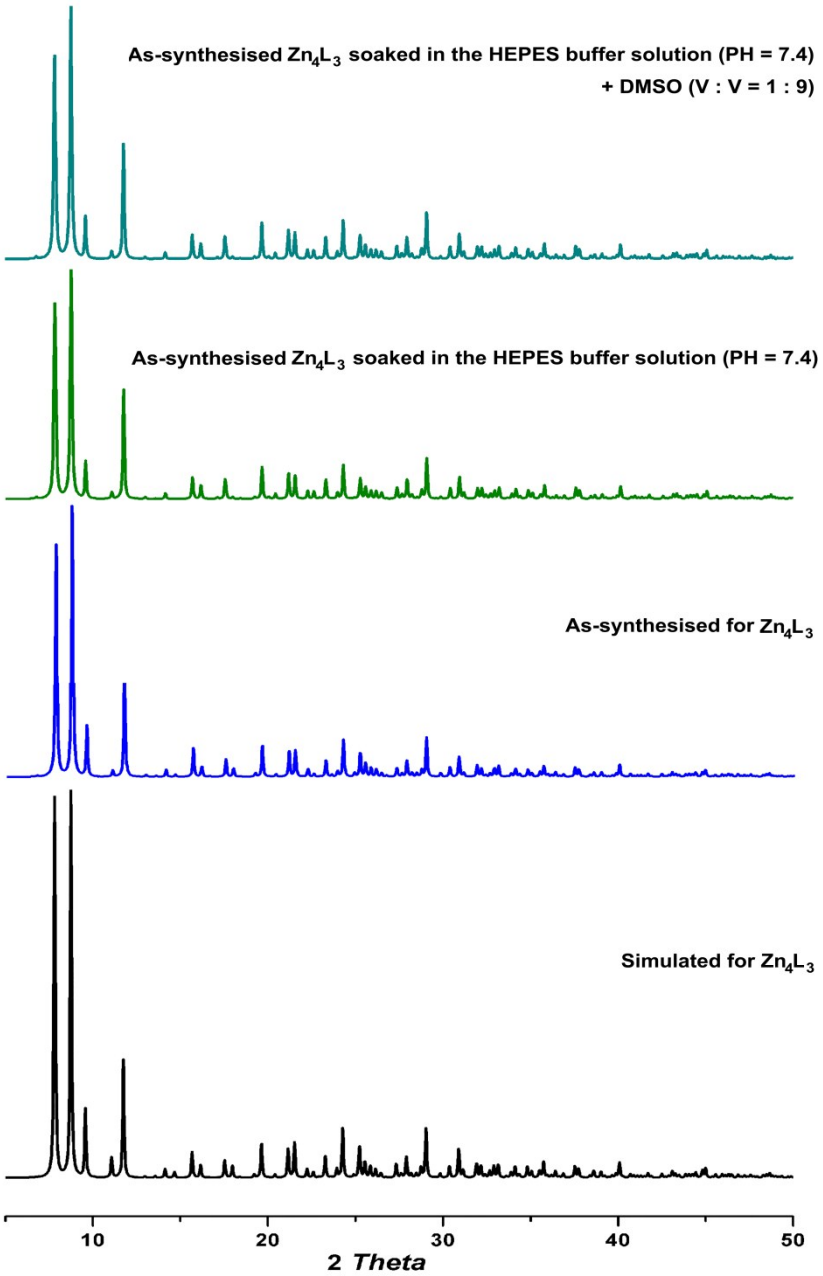

Figure S6 Comparing the simulated PXRD (black line) and experimental patterns of **Zn_4L_3** in the bulky samples and that soaked in HEPES buffer solution (pH = 7.4) and in mixed HEPES buffer solution (pH = 7.4) + DMSO (*V* : *V*= 1 : 9) solution.

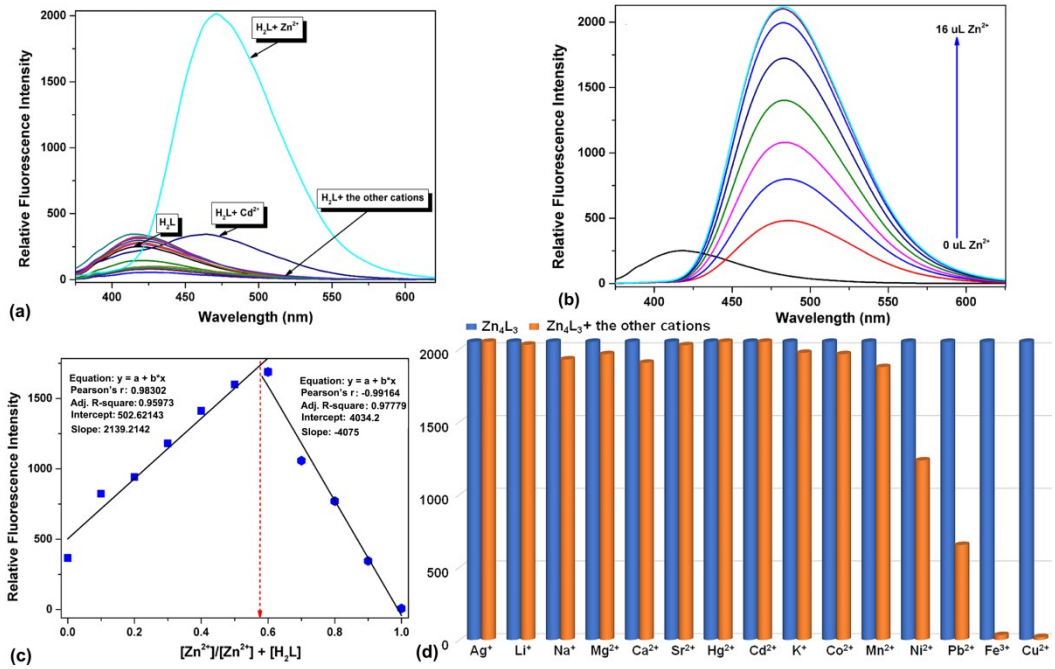

Figure S7 a) Fluorescence emission changes of H_2L (50 uM) upon addition of different cations in mixed HEPES buffer solution (pH = 7.4) + DMSO (*V* : *V*= 1 : 9) solution; b) Fluorescence emission changes of H_2L (50 uM) in mixed HEPES buffer solution (pH = 7.4) + DMSO (*V* : *V*= 1 : 9)solution upon addition of Zn^{2+}; c) The Job curves of Zn_4L_3 in HEPES buffer solution (pH = 7.4) + DMSO (*V* : *V*= 1 : 9); d) Fluorescence emission intensity of Zn_4L_3 at 472 nm in the absense / presence of different cations in HEPES buffer solution (pH = 7.4) + DMSO (*V* : *V*= 1 : 9).

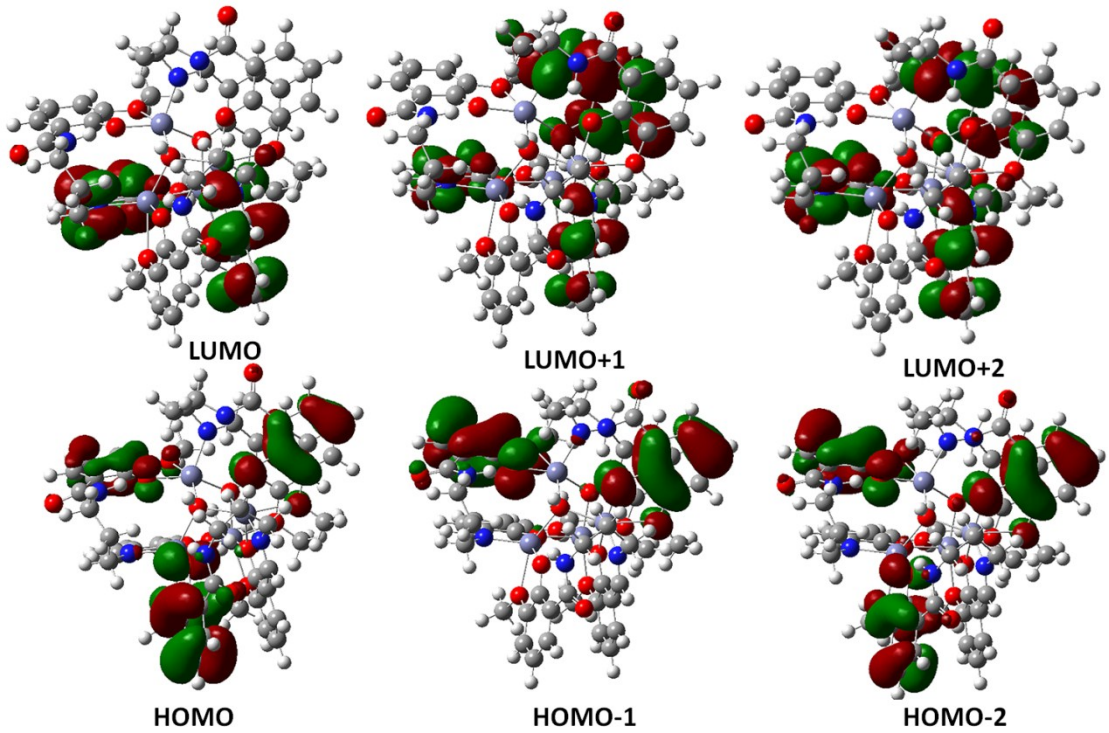

Figure S8 Contour plots of the frontier orbitals of **Zn_4L_3**.

The cartesian coordinate of the optimized structure of **Zn_4L_3** are as follows:
B3LYP/6-31G(d, p) + lanl2dz in gas phase, E = -4002 a.u., Charge = 1, Multiplicity = 1

Zn	1.401887	1.356539	-0.568369
Zn	0.000000	0.000000	2.204587
O	0.000000	0.000000	-1.136366
O	1.182919	-1.245533	1.183658
O	2.818400	0.316241	-1.367018
O	1.790363	-0.011935	3.397450
O	3.475311	1.852683	0.623686

N	2.140998	-2.947189	-0.998380
N	3.537702	-1.451435	-3.220774
H	3.040247	-0.771235	-3.050456
C	2.435533	-1.406155	1.625677
C	4.089985	0.325254	-1.019106
C	3.392488	-2.202361	0.987994
O	5.581986	-2.332511	-3.035156
C	2.808640	-0.742414	2.813922
C	4.512399	1.161008	0.044430
C	5.064310	-0.476796	-1.642991
C	5.815362	1.226698	0.447883
H	6.065873	1.791659	1.141742
C	4.080738	-0.820933	3.327475
H	4.304981	-0.362336	4.106494
C	6.392242	-0.402676	-1.200856
H	7.035797	-0.940376	-1.605232
C	4.677962	-2.292271	1.544040
H	5.311481	-2.840760	1.137874
C	4.749488	-1.490978	-2.688342
C	6.764811	0.434791	-0.196267
H	7.657711	0.480102	0.061751
C	5.023417	-1.592798	2.670970
H	5.894515	-1.636697	2.996538
C	2.102258	-3.892089	-2.139339
H	1.418835	-4.559690	-1.970406
H	2.956443	-4.349468	-2.197363
C	1.818397	-3.230292	-3.450964
H	1.099915	-2.590659	-3.324293
H	1.503644	-3.904894	-4.074329
C	3.773700	2.769859	1.656854
H	4.390321	3.429913	1.330882
H	4.167544	2.301346	2.395228
H	2.965406	3.200857	1.945183
C	3.004390	-2.504335	-4.082758
H	3.705750	-3.146284	-4.269935
H	2.726029	-2.114214	-4.926036
C	2.090762	0.781772	4.553305
H	1.307393	1.265562	4.822581
H	2.790277	1.403430	4.339974
H	2.378378	0.209483	5.267430
H	0.000000	0.000000	-1.937786
C	3.158021	-2.976220	-0.228598
H	3.835899	-3.563535	-0.473049
Zn	0.473854	-1.892339	-0.568369
O	-1.670123	-0.401672	1.183658
O	-1.135327	-2.598927	-1.367018
O	-0.905518	-1.544532	3.397450
O	-0.133185	-3.936049	0.623686
N	-3.622840	-0.380565	-0.998380
N	-3.025831	-2.338023	-3.220774
H	-2.188033	-2.247314	-3.050456
C	-2.435533	-1.406155	1.625677
C	-1.763314	-3.704657	-1.019106
C	-3.603545	-1.836800	0.987994
O	-4.811007	-3.667886	-3.035156
C	-2.047269	-2.061146	2.813922
C	-1.250737	-4.488356	0.044430
C	-2.945073	-4.147423	-1.642991
C	-1.845329	-5.649600	0.447883
H	-1.481314	-6.149030	1.141742
C	-2.751318	-3.123557	3.327475
H	-2.466283	-3.547055	4.106494
C	-3.544849	-5.334506	-1.200856
H	-4.332287	-5.622991	-1.605232
C	-4.324146	-2.905099	1.544040
H	-5.115910	-3.179498	1.137874
C	-3.665969	-3.367688	-2.688342
C	-3.005866	-6.075894	-0.196267
H	-3.413075	-6.871823	0.061751

C	-3.891112	-3.554007	2.670970
H	-4.364678	-4.286452	2.996538
C	-4.421777	0.125435	-2.139339
H	-4.658225	1.051098	-1.970406
H	-5.244971	-0.385620	-2.197363
C	-3.706714	0.040368	-3.450964
H	-2.793534	0.342775	-3.324293
H	-4.133560	0.650254	-4.074329
C	0.511918	-4.653049	1.656854
H	0.775232	-5.517086	1.330882
H	-0.090748	-4.759871	2.395228
H	1.289320	-4.168545	1.945183
C	-3.671013	-1.349711	-4.082758
H	-4.577636	-1.636131	-4.269935
H	-3.193978	-1.303703	-4.926036
C	-0.368346	-2.201539	4.553305
H	0.442312	-1.765017	4.822581
H	-0.179732	-3.118166	4.339974
H	-1.007771	-2.164477	5.267430
C	-4.156493	-1.246816	-0.228598
H	-5.004062	-1.540218	-0.473049
Zn	-1.875740	0.535800	-0.568369
O	0.487204	1.647205	1.183658
O	-1.683073	2.282686	-1.367018
O	-0.884845	1.556467	3.397450
O	-3.342126	2.083366	0.623686
N	1.481841	3.327753	-0.998380
N	-0.511872	3.789458	-3.220774
H	-0.852214	3.018549	-3.050456
C	0.000000	2.812311	1.625677
C	-2.326670	3.379404	-1.019106
C	0.211057	4.039161	0.987994
O	-0.770979	6.000398	-3.035156
C	-0.761371	2.803561	2.813922
C	-3.261662	3.327348	0.044430
C	-2.119237	4.624219	-1.642991
C	-3.970033	4.422902	0.447883
H	-4.584559	4.357371	1.141742
C	-1.329421	3.944489	3.327475
H	-1.838698	3.909391	4.106494
C	-2.847393	5.737182	-1.200856
H	-2.703509	6.563366	-1.605232
C	-0.353816	5.197370	1.544040
H	-0.195571	6.020257	1.137874
C	-1.083519	4.858666	-2.688342
C	-3.758945	5.641103	-0.196267
H	-4.244636	6.391722	0.061751
C	-1.132305	5.146805	2.670970
H	-1.529837	5.923148	2.996538
C	2.319519	3.766653	-2.139339
H	3.239390	3.508592	-1.970406
H	2.288529	4.735088	-2.197363
C	1.888317	3.189924	-3.450964
H	1.693619	2.247884	-3.324293
H	2.629916	3.254641	-4.074329
C	-4.285618	1.883191	1.656854
H	-5.165552	2.087172	1.330882
H	-4.076796	2.458526	2.395228
H	-4.254726	0.967689	1.945183
C	0.666623	3.854045	-4.082758
H	0.871887	4.782415	-4.269935
H	0.467949	3.417917	-4.926036
C	-1.722416	1.419767	4.553305
H	-1.749706	0.499455	4.822581
H	-2.610545	1.714735	4.339974
H	-1.370607	1.954994	5.267430
C	0.998472	4.223036	-0.228598
H	1.168163	5.103754	-0.473049

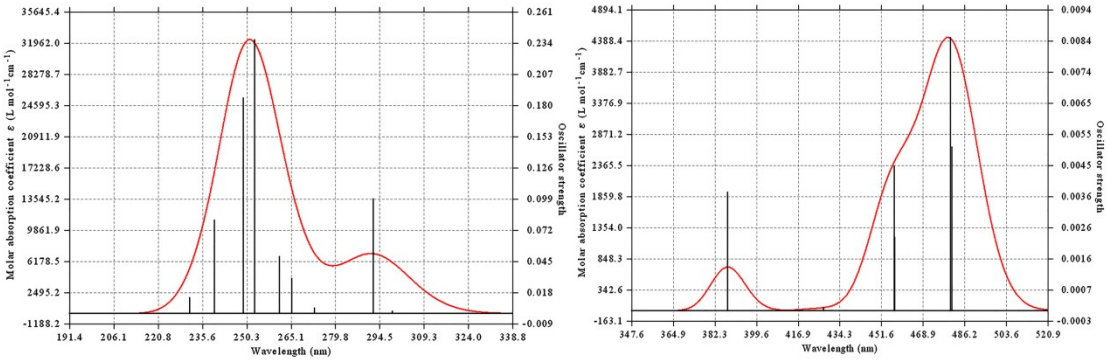

Figure S9 The simulated fluorescence spectrum H_2L and Zn_4L_3 based on TD-DFT calculations.

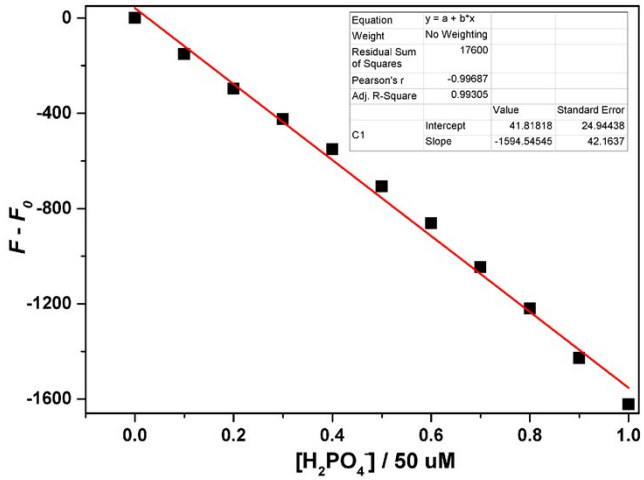

Figure S10. Linear concentration range of $\mathbf{Zn_4L_3}$ (50 uM) with $H_2PO_4^-$ in HEPES (pH=7.4) + DMSO (V : V = 1 : 9) solution (λ_{em} = 472 nm).

The result of the analysis as follows:

Linear Equation: Y = – 213.56 X – 14.61, R = 0.99288 $\partial = \sqrt{\frac{(F_0 - \overline{F_0})^2}{n-1}}$ =1.58, n = 10, K = 3

LOD = K × δ / Slope = 3 × 1.58 /1594.54 = 1.50 × 10^{-7} M = 0.15 uM

F_0 is the fluorescence intensity at 472 nm of $\mathbf{Zn_4L_3}$.

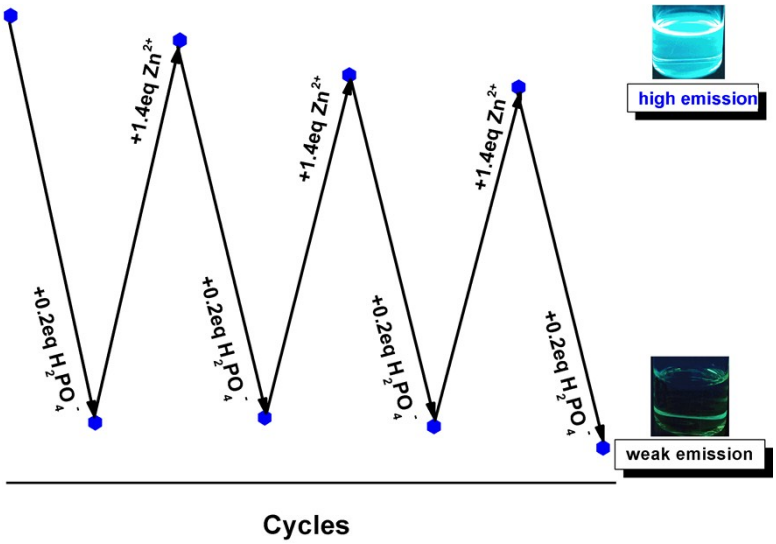

Figure S11 Relative emission intensity of **Zn_4L_3** at 472 nm upon adding $Zn^{2+}/H_2PO_4^-$ in HEPES (pH=7.4) + DMSO (V : V = 1 : 9) solution.

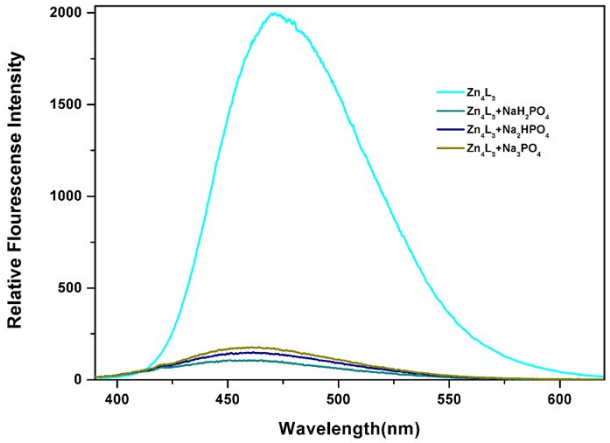

Figure S12 Emission spectra of **Zn_4L_3** upon addition of 0.2 equiv. of $NaH_2PO_4/Na_2HPO_4/Na_3PO_4$ in HEPES (pH=7.4) + DMSO (V : V = 1 : 9) solution (λ_{em} = 472 nm).

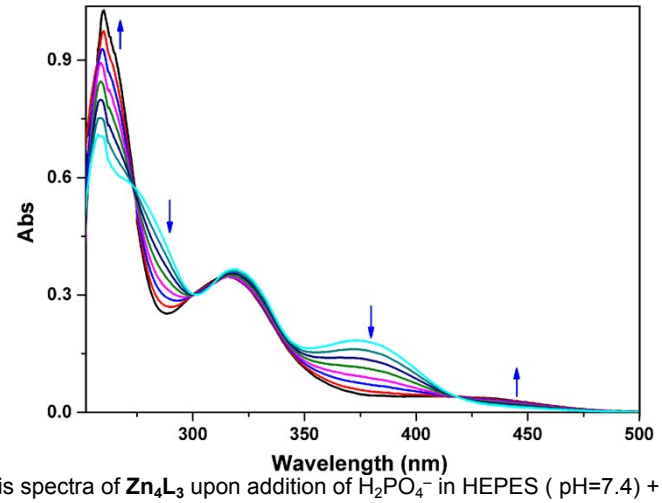

Figure S13. UV-Vis spectra of **Zn_4L_3** upon addition of $H_2PO_4^-$ in HEPES (pH=7.4) + DMSO (*V* : *V* =1 : 9) solution.