Supporting Information

for

A bio-attuned ratiometric hydrogen sulfate ion selective receptor in aqueous solvent: structural proof of the H-bonded adduct

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CONTENTS

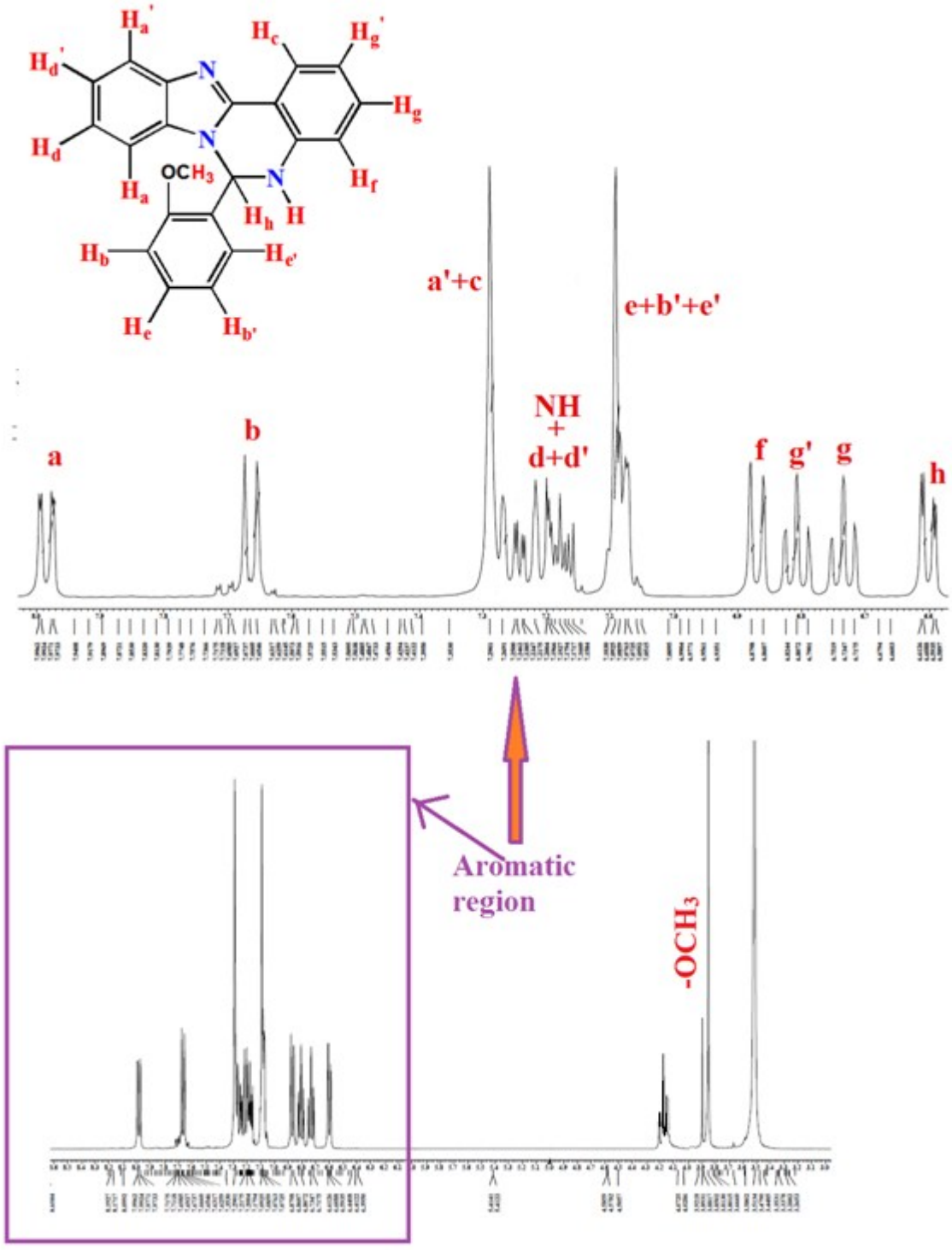

Fig. S1 ^{1}HNMR of **1** (with expansion) in DMSO-d_6

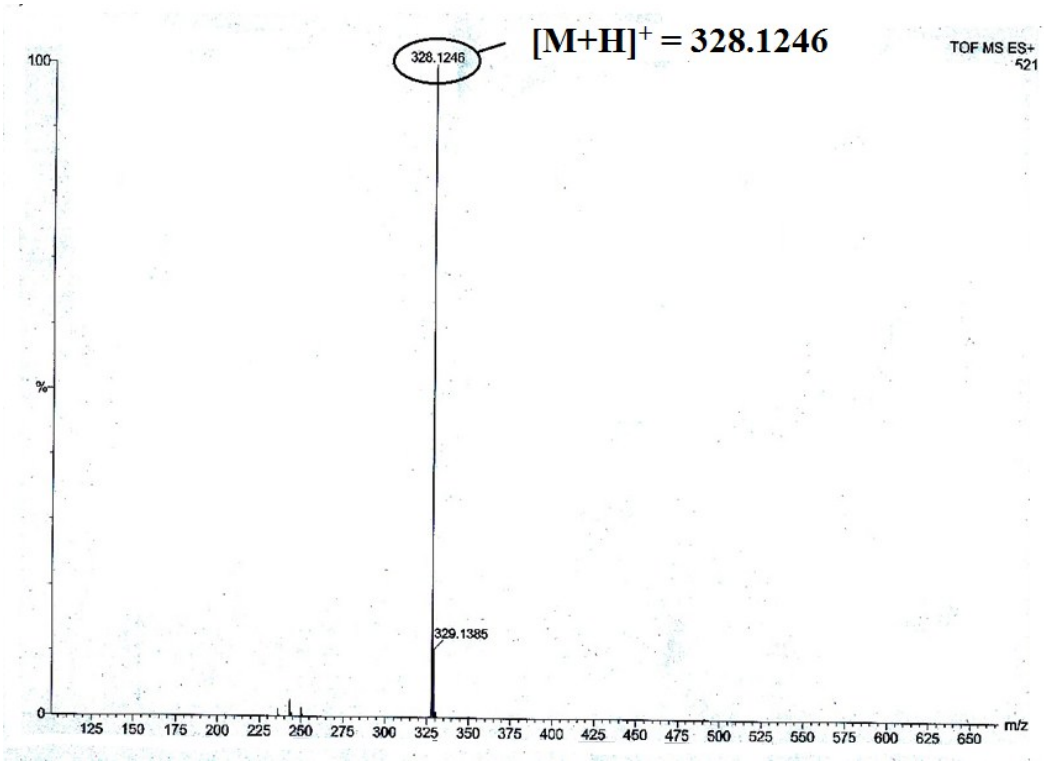

Fig. S2 Mass spectrum of **1**

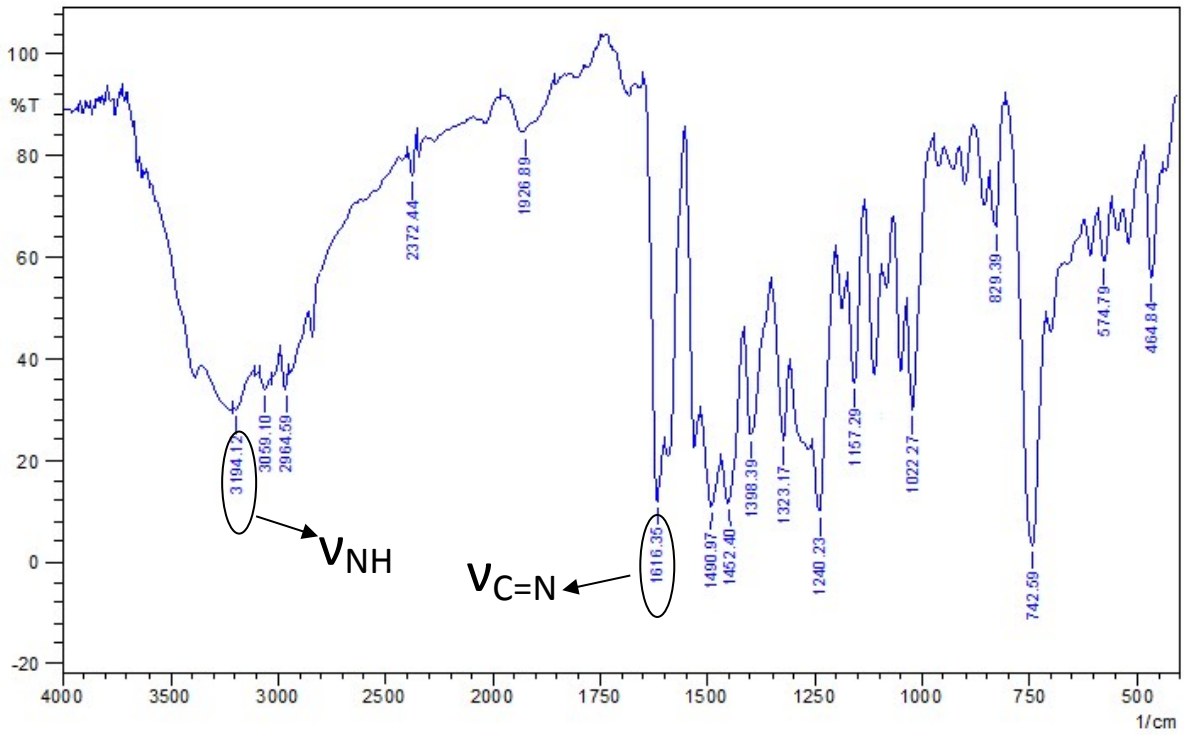

Fig. S3 IR spectrum of **1**

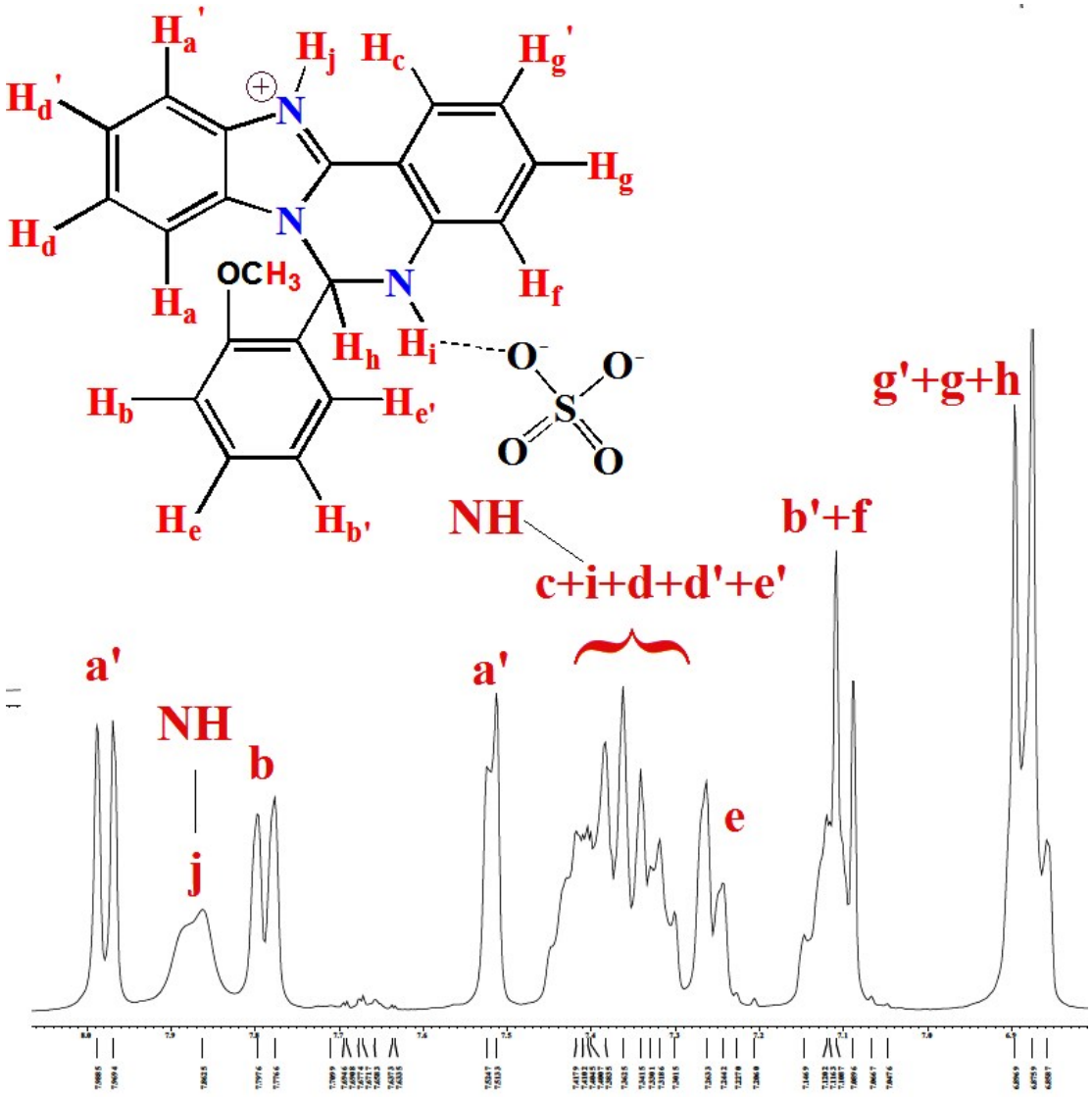

Fig. S4 ^{1}H NMR spectrum of **2** in DMSO-d_6

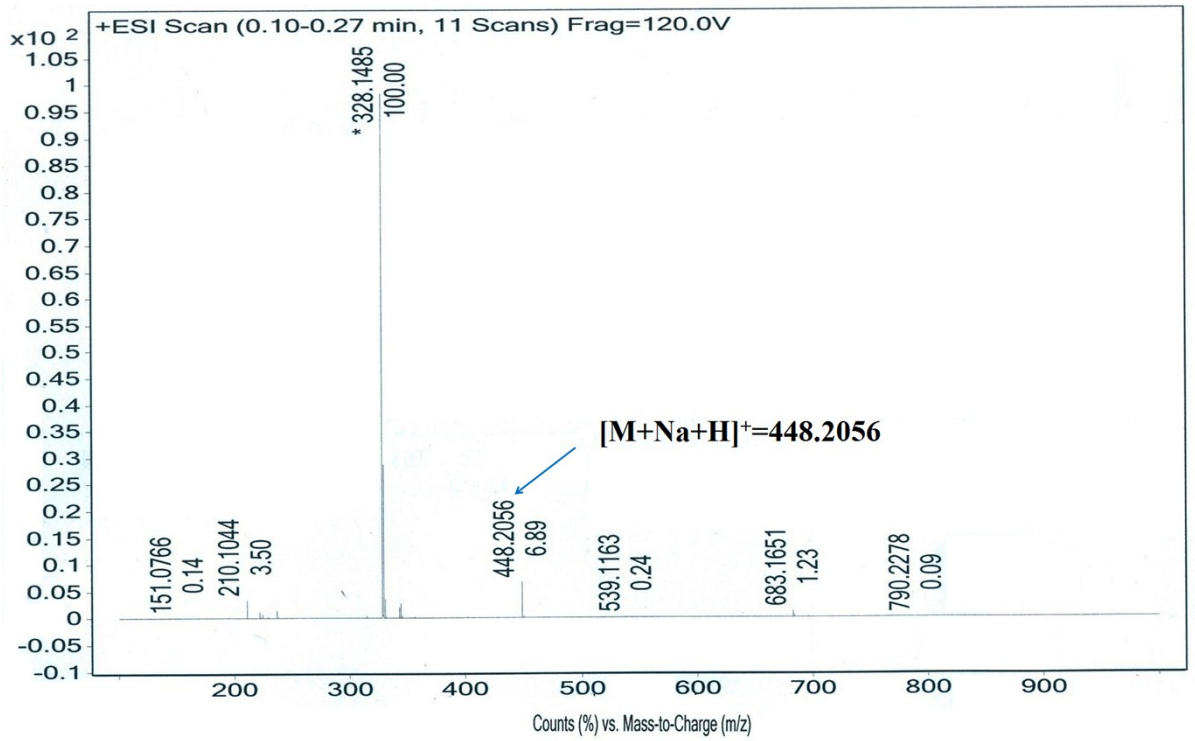

Fig. S5 Mass spectrum of $[LHSO_4]^-LH^+.3H_2O$ **(2)**

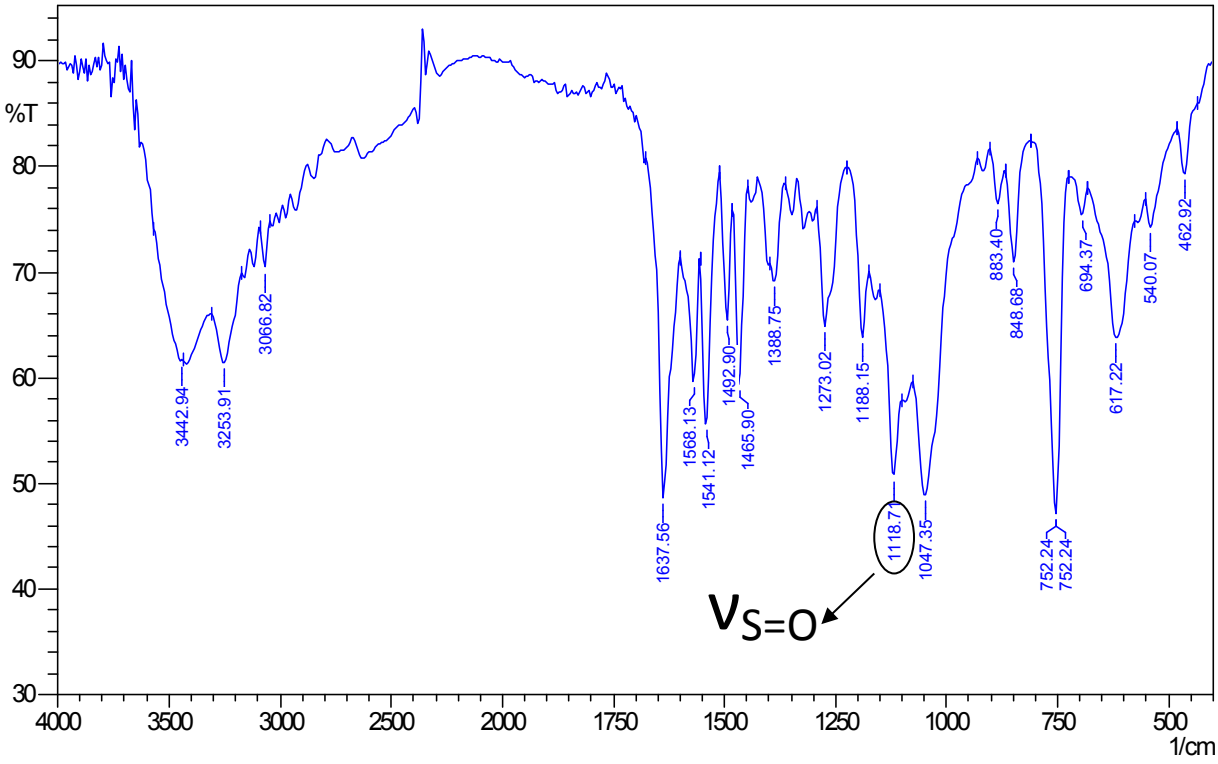

Fig. S6 IR spectrum of **2**

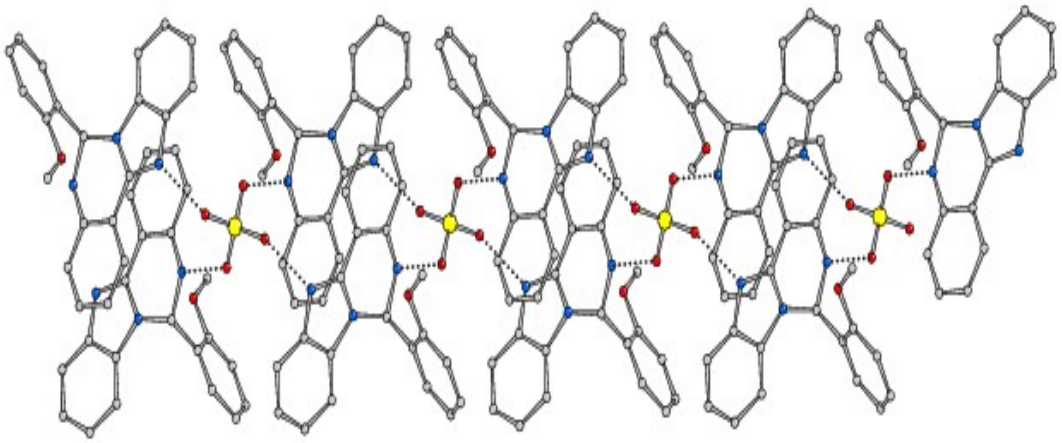

Fig. S7 Crystal packing of compound **2** showing the polymeric chain running along the [101] direction realized by $O_3SO\ldots HN$ hydrogen bonds

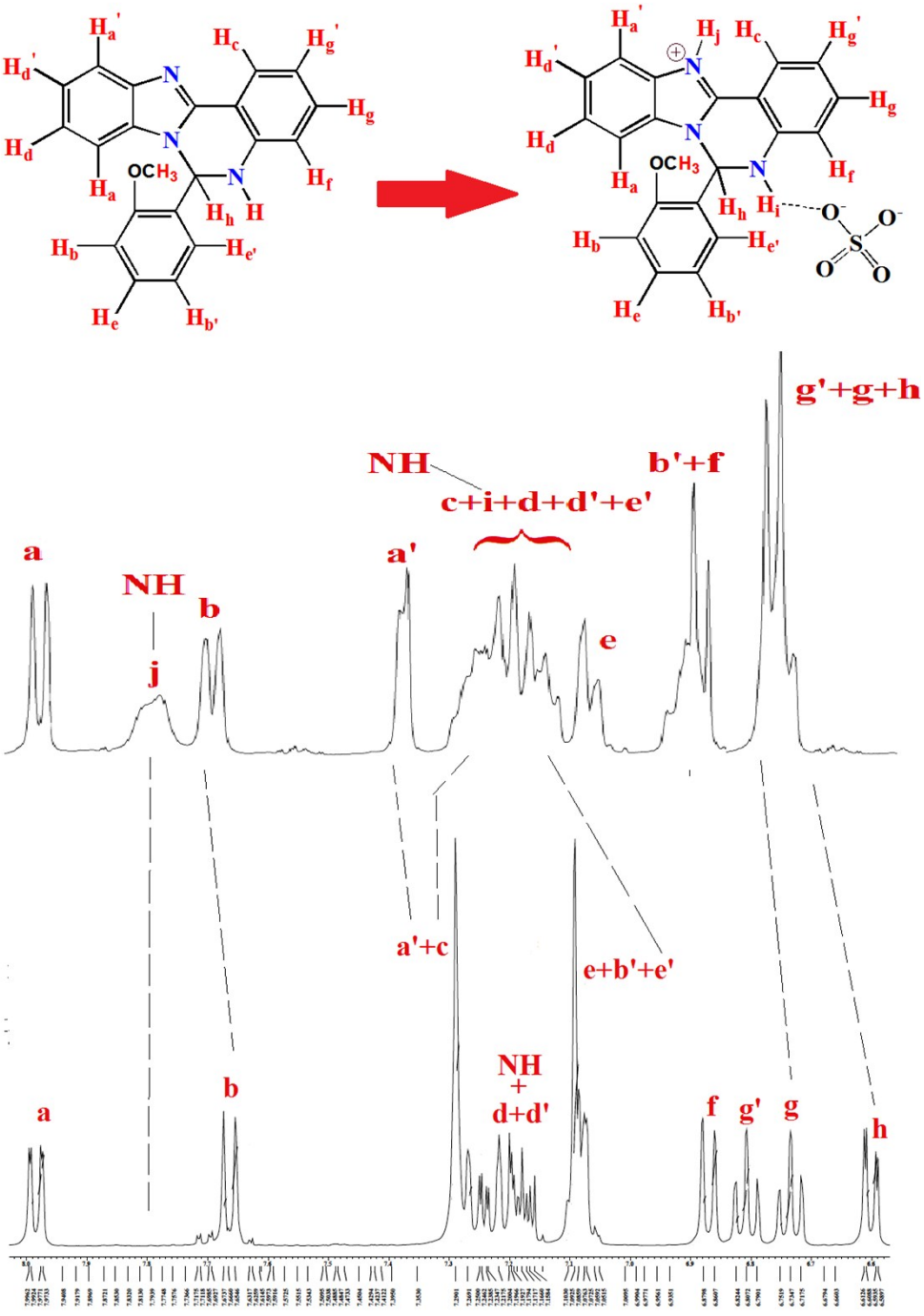

Fig. S8 ^{1}H NMR ~~spectrum of~~ titration of **1** with HSO_4^- in DMSO-d_6

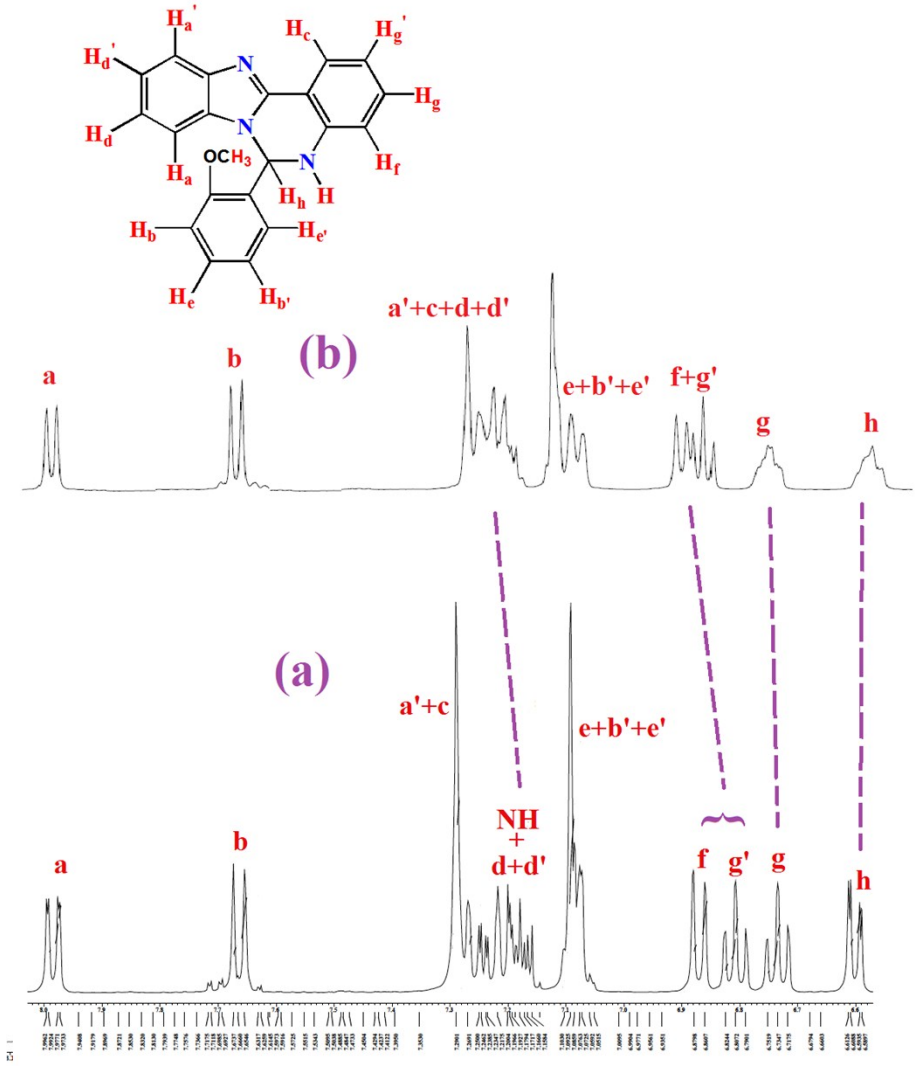

Fig. S9 ^{1}H NMR ~~spectrum of~~ **1 (a)** in absence and **(b)** in presence of D_2O

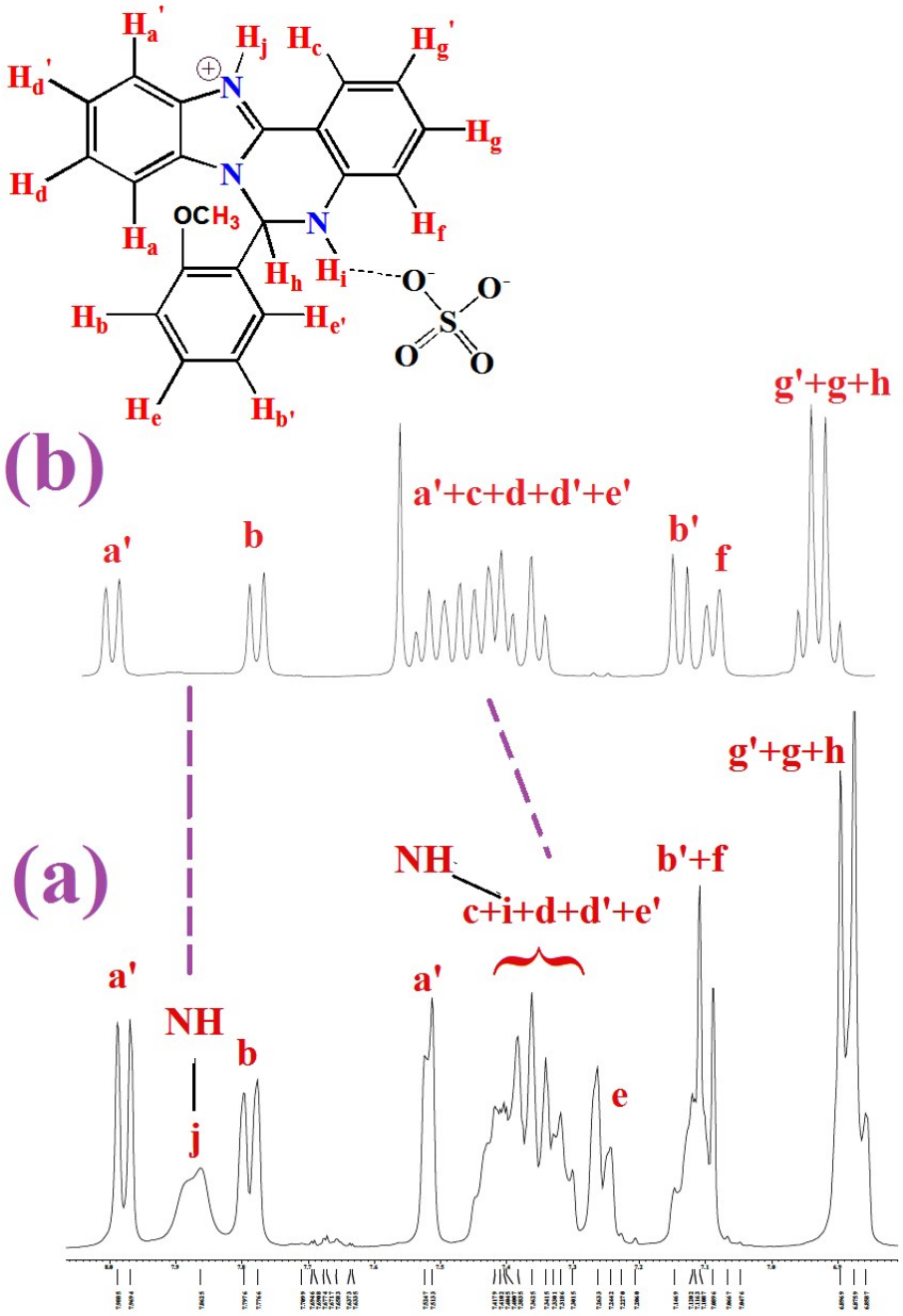

Fig. S10 ^{1}H NMR spectrum of **2 (a)** in absence and **(b)** in presence of D_2O

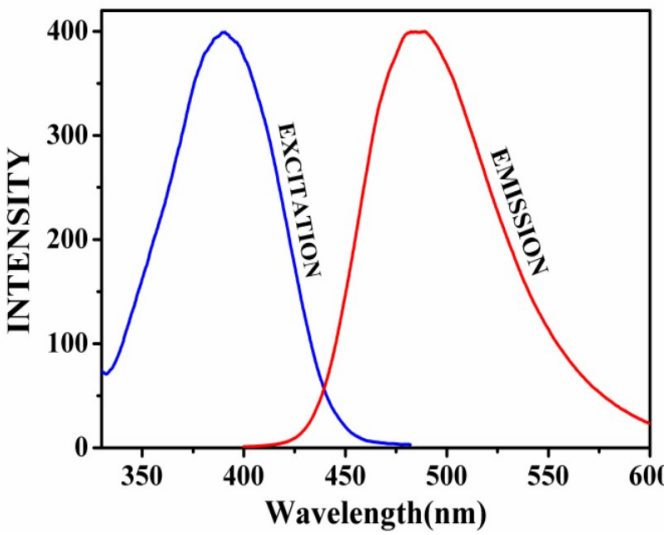

Fig. S11 Absorption and emission spectra of 25 μM of **1** in 100 mM HEPES buffer (ethanol/water 1:5, v/v) at 25 °C

Fig. S12 Fluorescence colour of **1** in absence (left) and presence (right) of HSO_4^- ions.

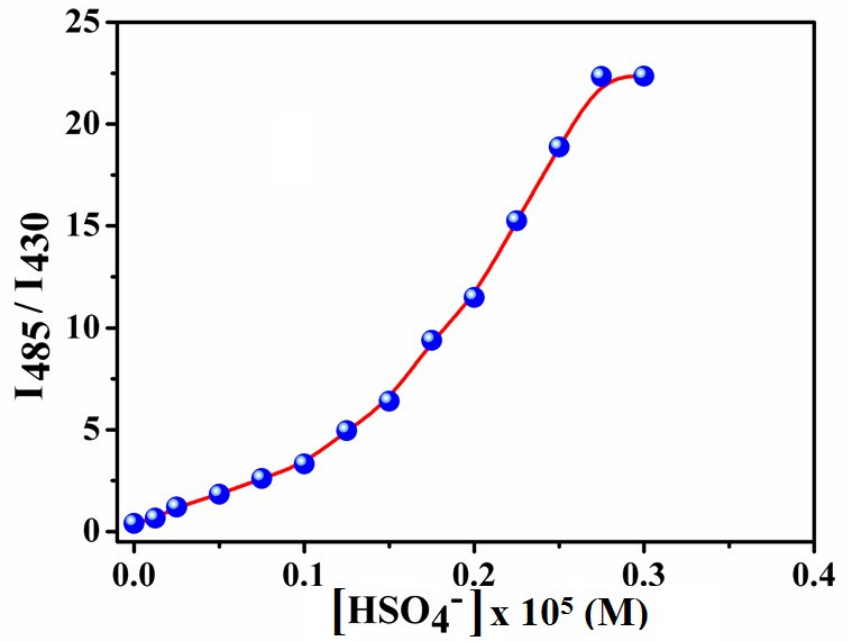

Fig. S13 Ratiometric signaling of fluorescence output of **1**

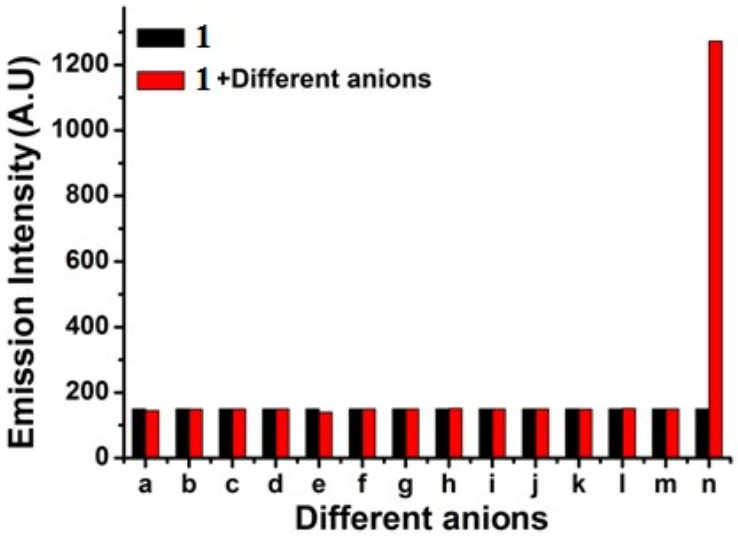

Fig. S14.Fluorescence intensity of **1** in presence of different anions in HEPES buffer (100 mM, pH 7.4; ethanol/water: 1/5, v/v) at 25 °C, (a) Cl^-, (b) Br^-, (c) I^-, (d) F^-, (e) OAc^-, (f) $H_2PO_4^-$, (g) N_3^-, (h) ClO_4^-, (i) $H_2AsO_4^-$, (j) SO_4^{2-}, (k) S^{2-}, (l) CN^-, (m) NO_3^-, (n) HSO_4^- ions

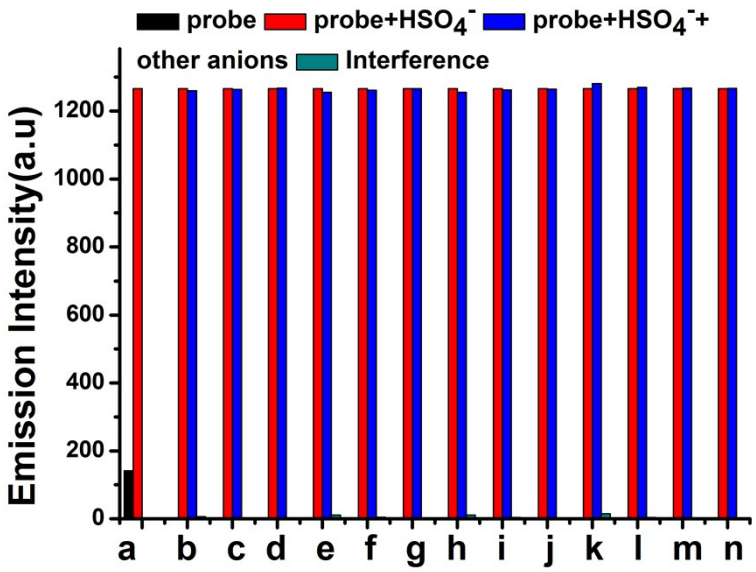

Fig. S15 Change of relative fluorescence intensity profile of **1** in presence of different anions in ethanol: water (1: 5, v/v) at room temperature (λ_{ex}= 390 nm) (a) HSO_4^-, (b) Cl^-, (c) Br^-, (d) I^-, (e) F^-, (f) OAc^-, (g) $H_2PO_4^-$, (h) $H_2AsO_4^-$, (i) ClO_4^-, (j) N_3^-, (k) SO_4^{2-}, (l) S^{2-}, (m) CN^-, (n) NO_3^- ions.

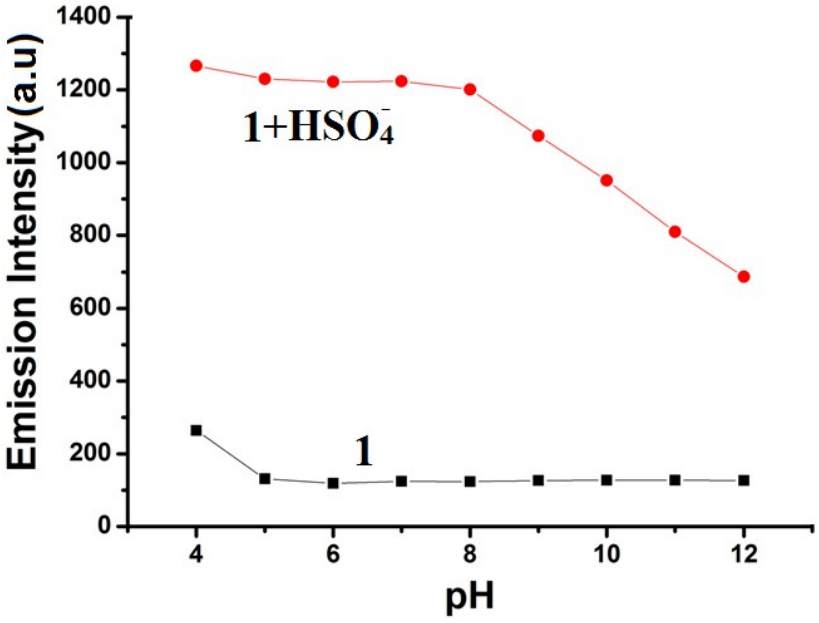

Fig. S16 Fluorescence response of **1** (25 μM) in absence and in presence of HSO_4^- (one equivalent) at different pH in 100 mM HEPES buffer (ethanol/ water: 1/5) at 25 °C.

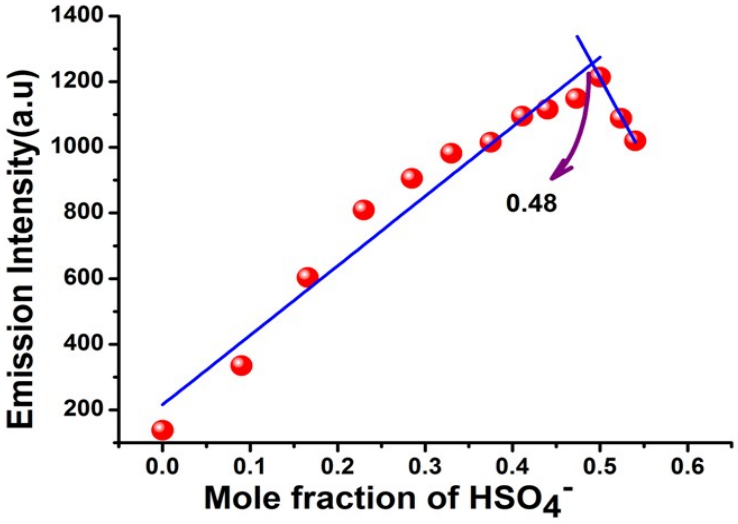

Fig. S17 Job's plot of **1** showing maxima at 1:1

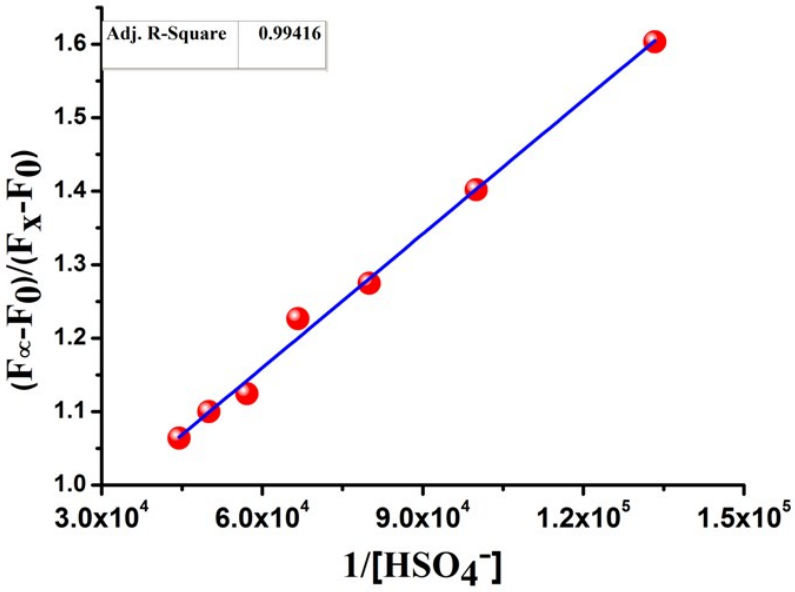

Fig. S18 Binding constant value K = 1.648 x 10^5 M^{-1} for **1** determined from the intercept/slope of the plot.

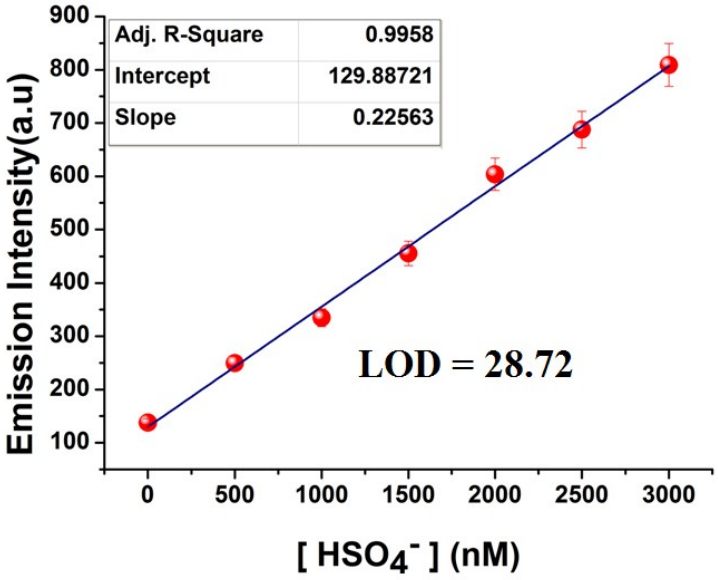

Fig. S19 Calibration curve for the nanomolar range, with error bars for calculating the LOD of HSO_4^- by **1** in 100 mM HEPES buffer (ethanol / water: 1/5) at 25 °C.

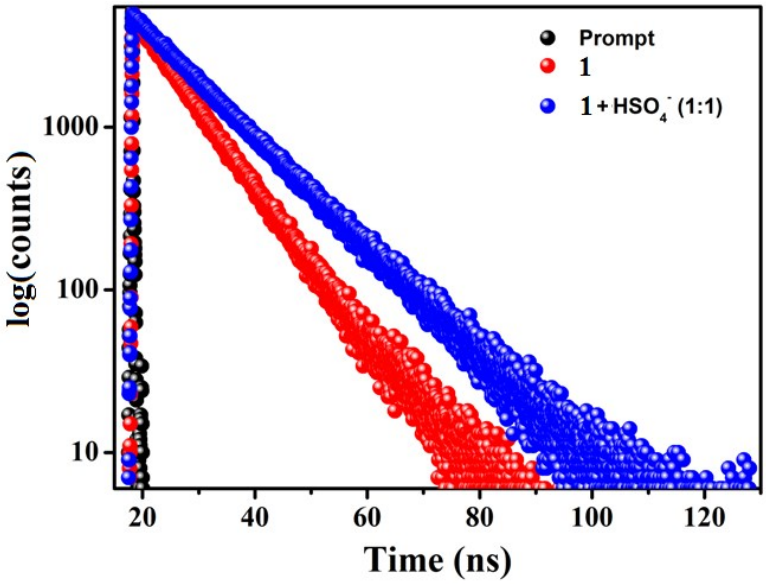

Fig. S20 Time-resolved fluorescence decay of **1** (10 mM) in the absence and presence of added HSO_4^- ions (10 mM) at λ_{ex} = 390 nm in 100 mM HEPES buffer (ethanol/ water: 1/5, v/v) [λ_{em}: 485 nm].

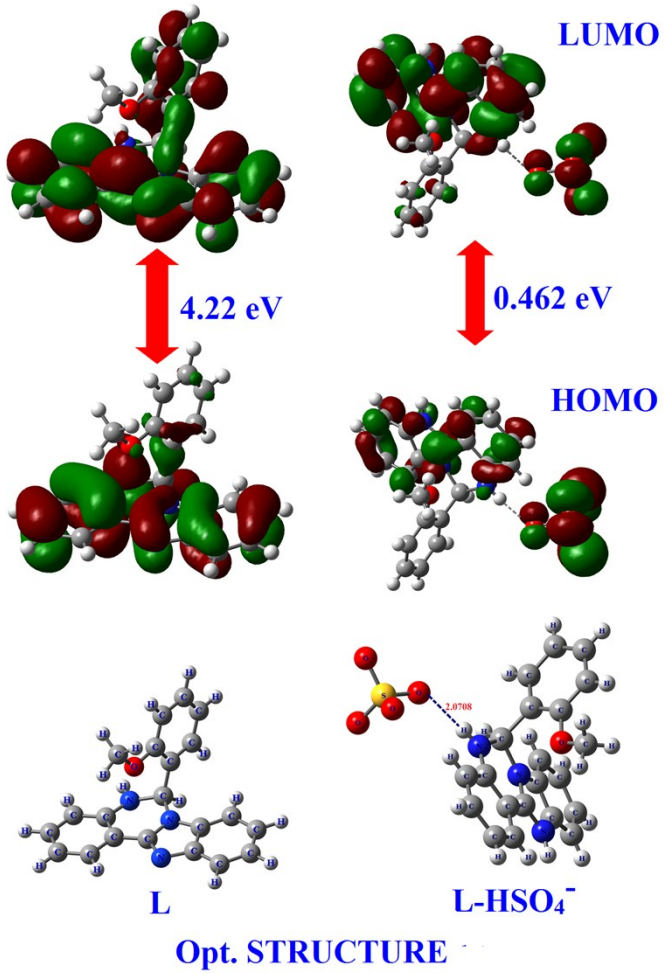

Fig. S21 Optimised structure and energy level diagram for the frontier π-MOs of **1** (left) and complex **2** (right).

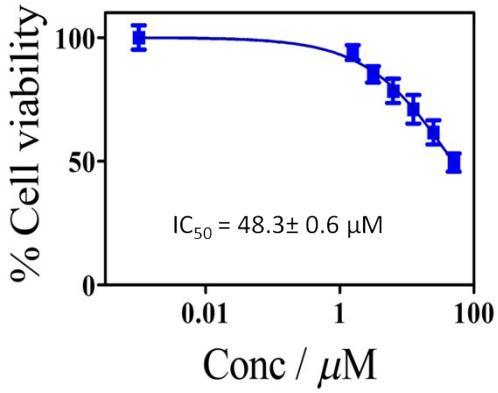

Fig. S22 Cytotoxic effect of **1** (5, 10, 25, 50 and 100 μM) in HeLa cells incubated for 18 h

Table S1 Crystal data and details of refinements for **2**

Empirical Formula	$2(C_{21}H_{18}N_3O).SO_4.3H_2O$
Formula Weight	806.88
Crystal system	monoclinic
Space group	*C* 2/c
a (Å)	16.3414(8)
b (Å)	17.0145(9)
c (Å)	16.3578(11)
β (°)	118.819(3)
Volume ($Å^3$)	3984.8(4)
Temperature (K)	296(2)
ρ_{calc} (g/cm^3)	1.345
μ (mm^{-1})	0.146
Z	4
F(000)	1696
θ range (deg)	3.46- 21.51
No. of reflns total	2290
No. of reflns [I > 2σ(I)]	1674
Goodness-of-fit on F^2	1.072
*R*1, *wR*2 (*I* >2σ(*I*))	0.0558, 0.1513
*R*1, *wR*2 (all data)	0.0800, 0.1726

Table S2 Selected bond distances (Å) and bond angles (°) for **2**

Bond length (Å)	
N1 C15	1.333(5)
N1 C16	1.397(5)
N2 C15	1.347(5)
N2 C21	1.402(5)
N2 C8	1.465(5)
N3 C9	1.363(5)
N3 C8	1.443(5)
O1 C2	1.365(5)
O1 C1	1.414(5)
Bond angles (°)	
C15 N1 C16	109.2(3)
C15 N2 C21	108.4(3)
C15 N2 C8	124.8(3)
C21 N2 C8	126.5(3)
C9 N3 C8	125.4(3)
C2 O1 C1	119.1(3)
N3 C8 N2	107.9(3)
N3 C8 C7	115.4(3)
O1 C2 C7	115.6(3)
N3 C9 C10	120.8(4)
N3 C9 C14	120.8(4)
C10 C9 C14	118.3(4)
N1 C15 N2	109.0(4)
N1 C15 C14	129.3(4)
N2 C15 C14	121.7(4)

Table S3. Life time details of **1**

	B_1	B_2	τ_1 (ns)	τ_2 (ns)	τ_{av} (ns)	χ^2	Φ	K_r	K_{nr}
1	56.17	43.83	7.71	10.74	9.038	1.068	0.07	0.0077	0.1028
1+HSO_4^- (1:1)	5.71	94.29	7.5	13.08	12.76	1.078	0.5	0.039	0.039