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Supporting Information

Coumarin based dual switching fluorescent 'turn-on' chemosensor for selective detection of Zn^{2+} and HSO_4^-: An experimental and theoretical study

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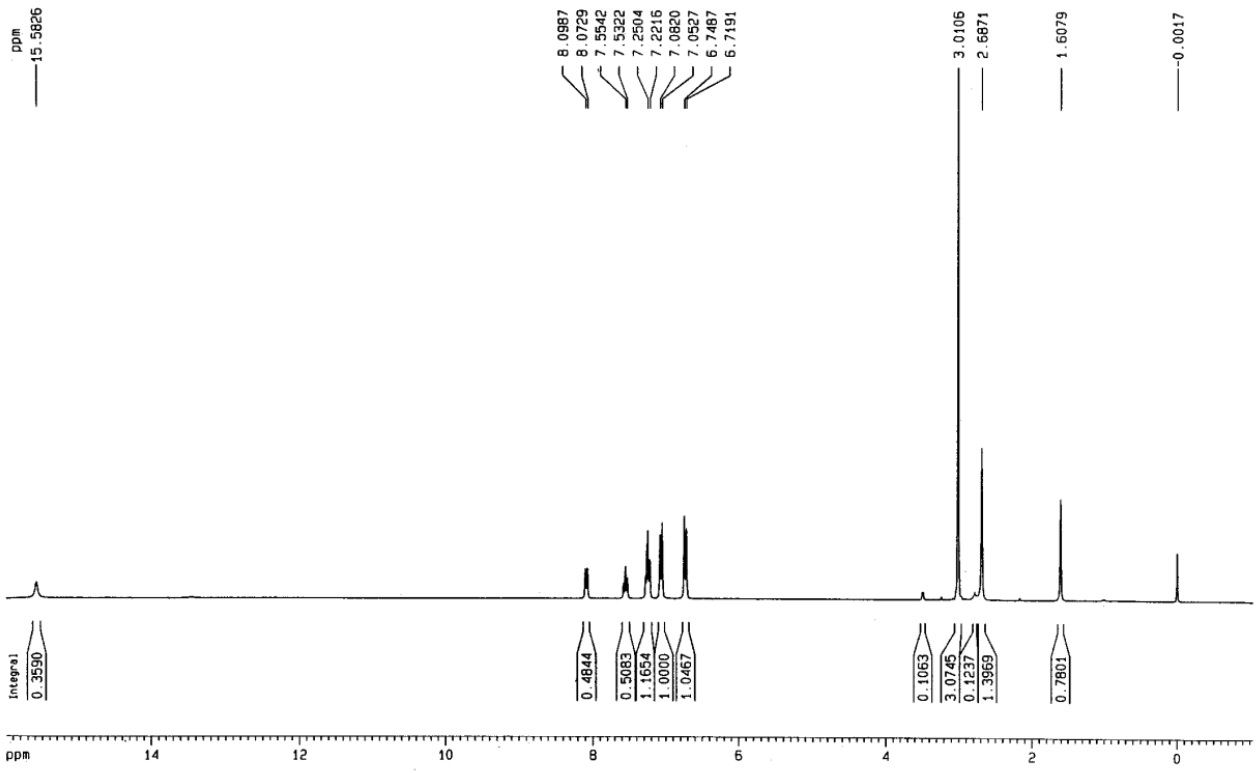


Fig. S1. ^{1}H-NMR spectra of HL in $CDCl_3$

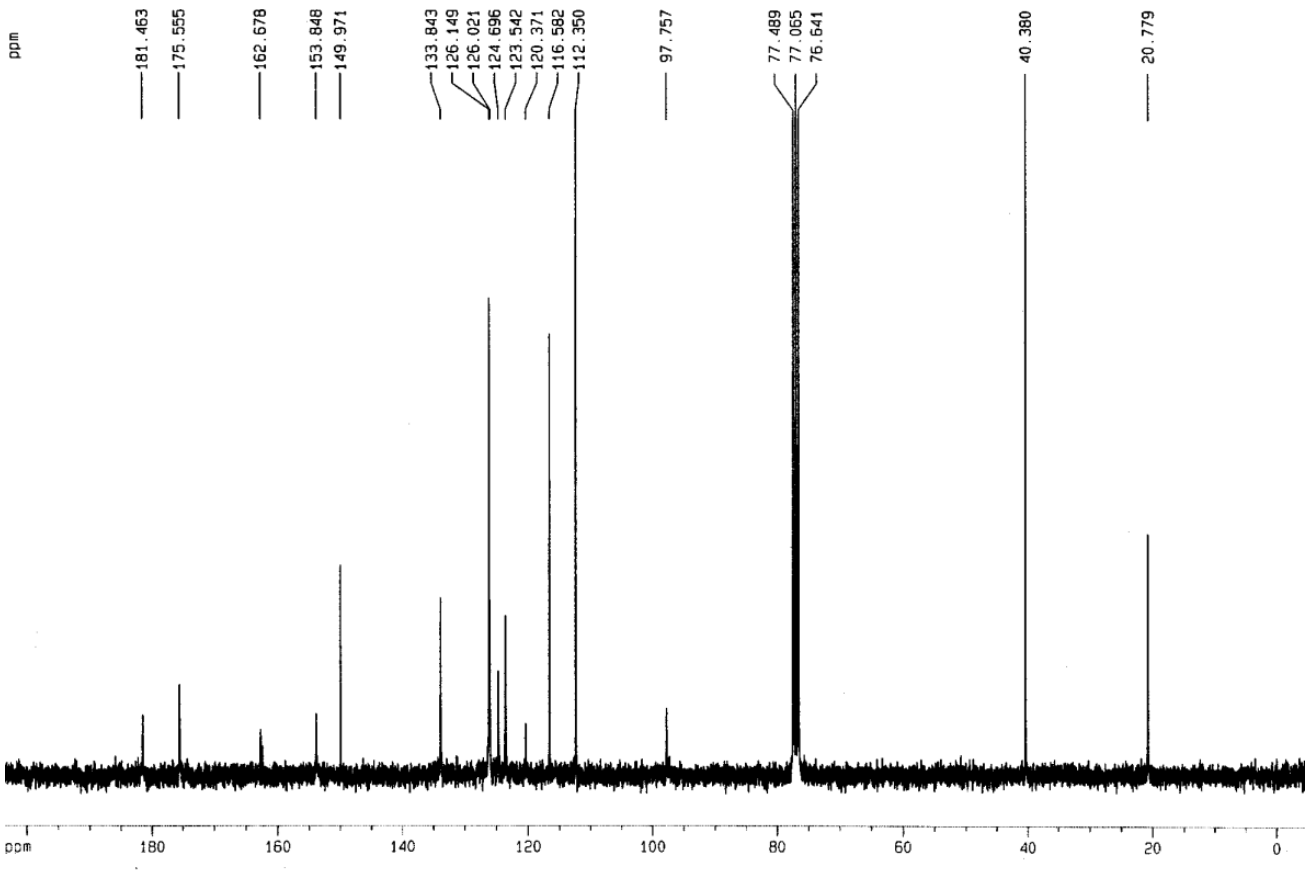


Fig. S2. ^{13}C-NMR spectrum of HL in $CDCl_3$

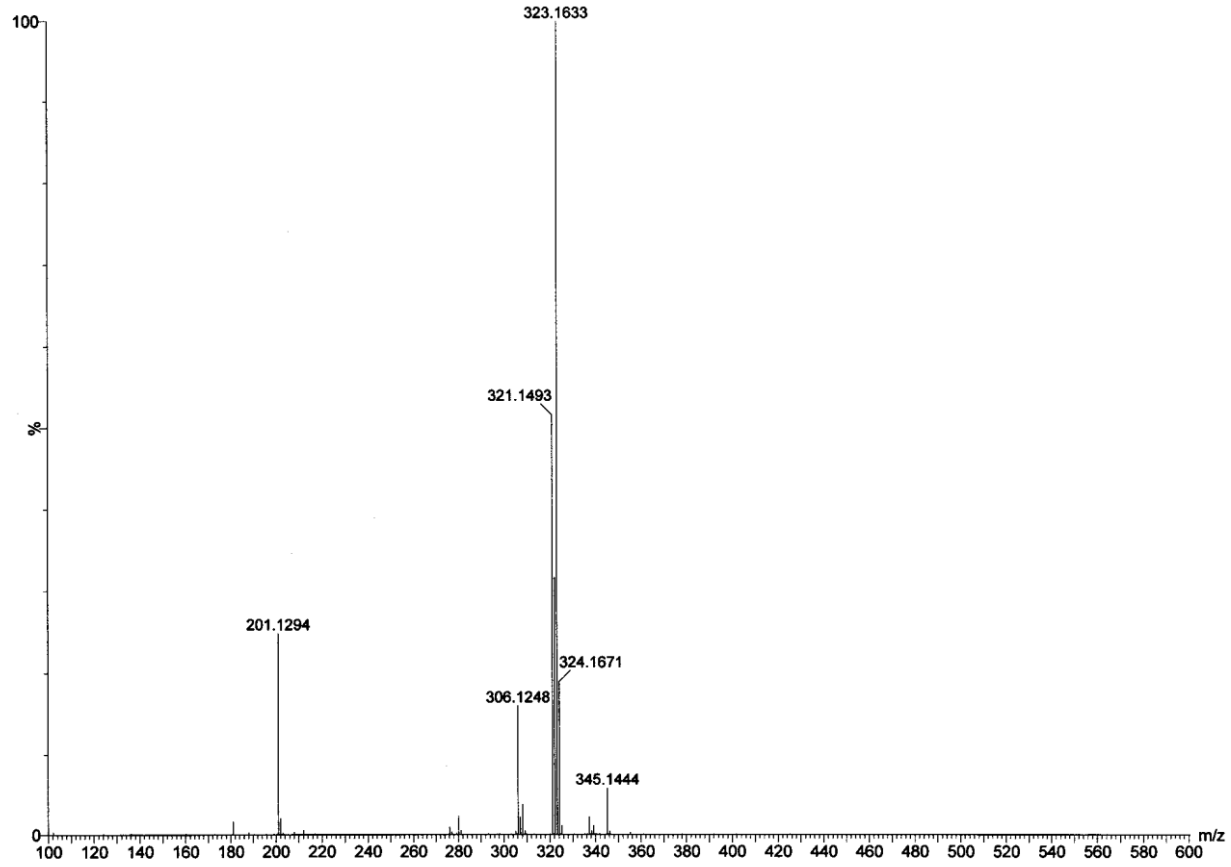


Fig. S3. ESI-MS spectra of the receptor HL

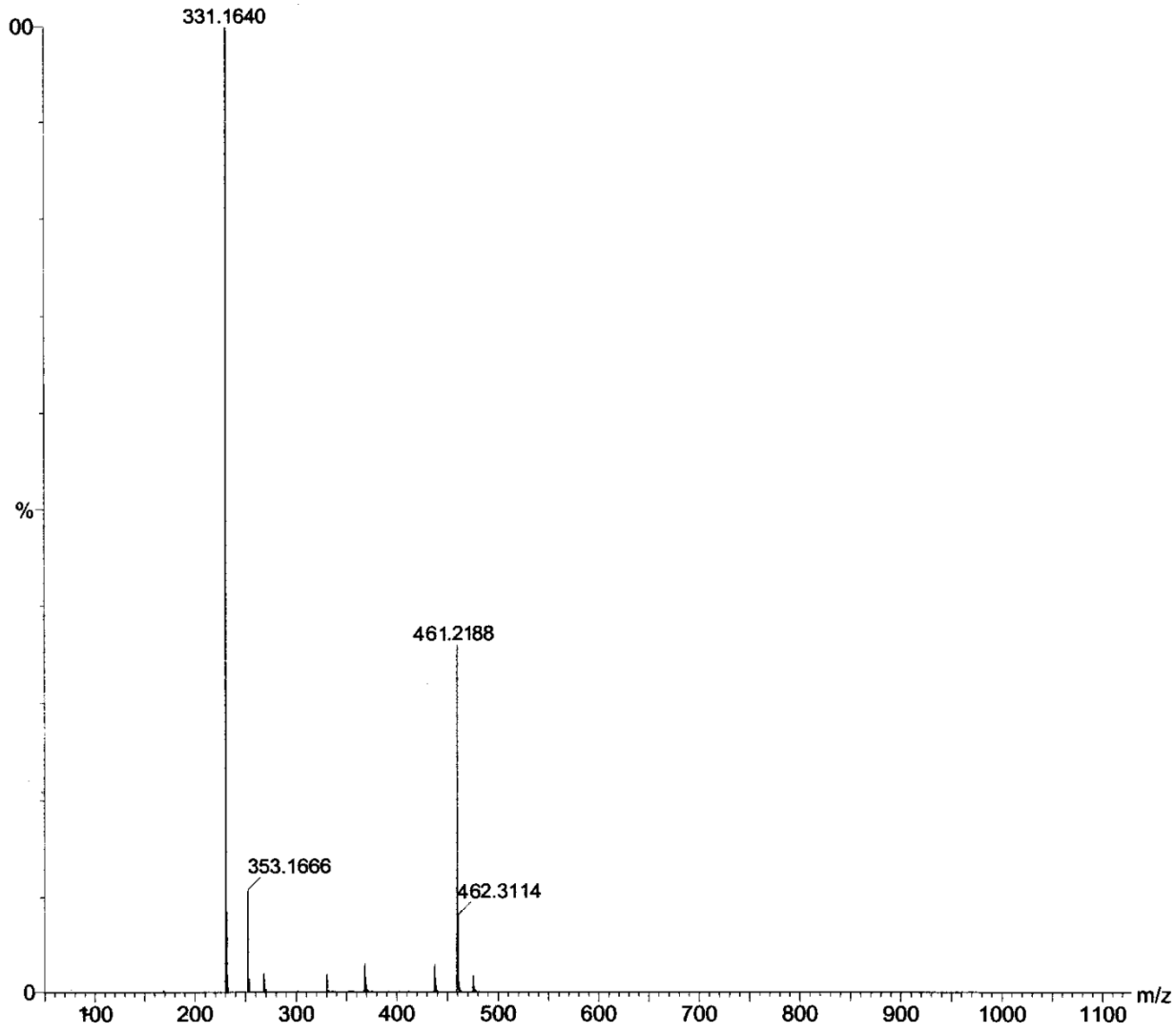


Fig. S4. ESI-MS spectra of the receptor HL-Zn^{2+} complex

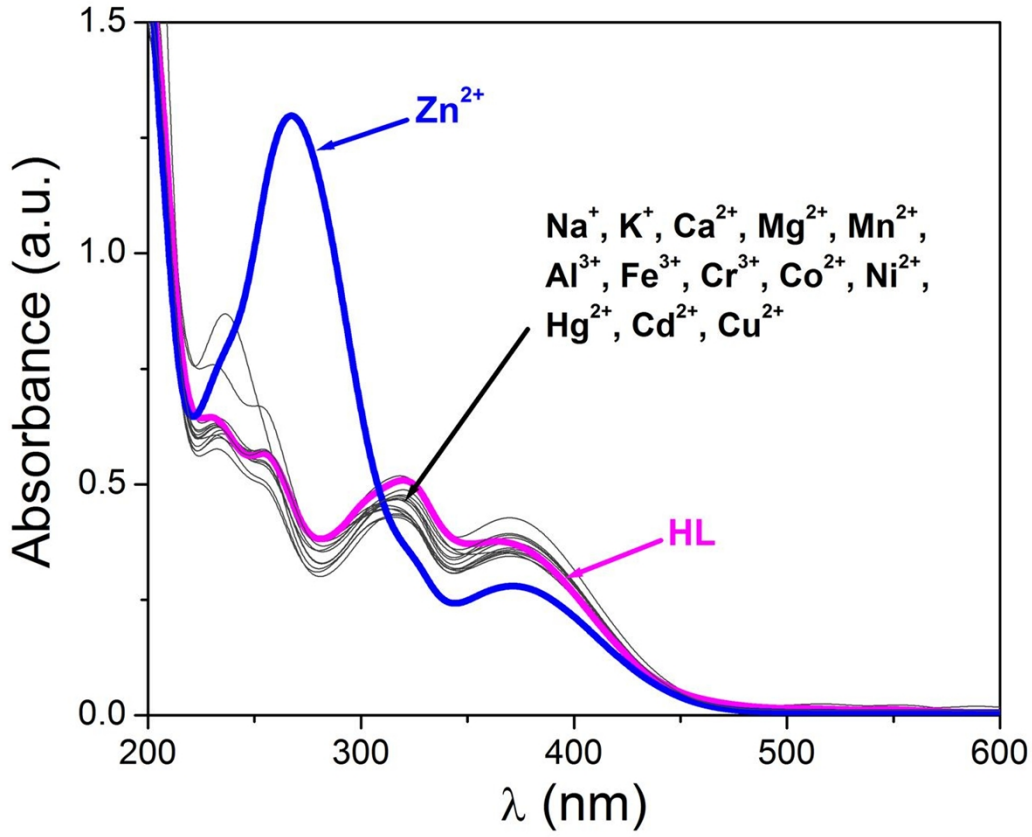


Fig. S5. UV-Vis spectra of chemosensor (HL) (10 μM) upon addition of 2 equivalent of various metal ions (100 μM).

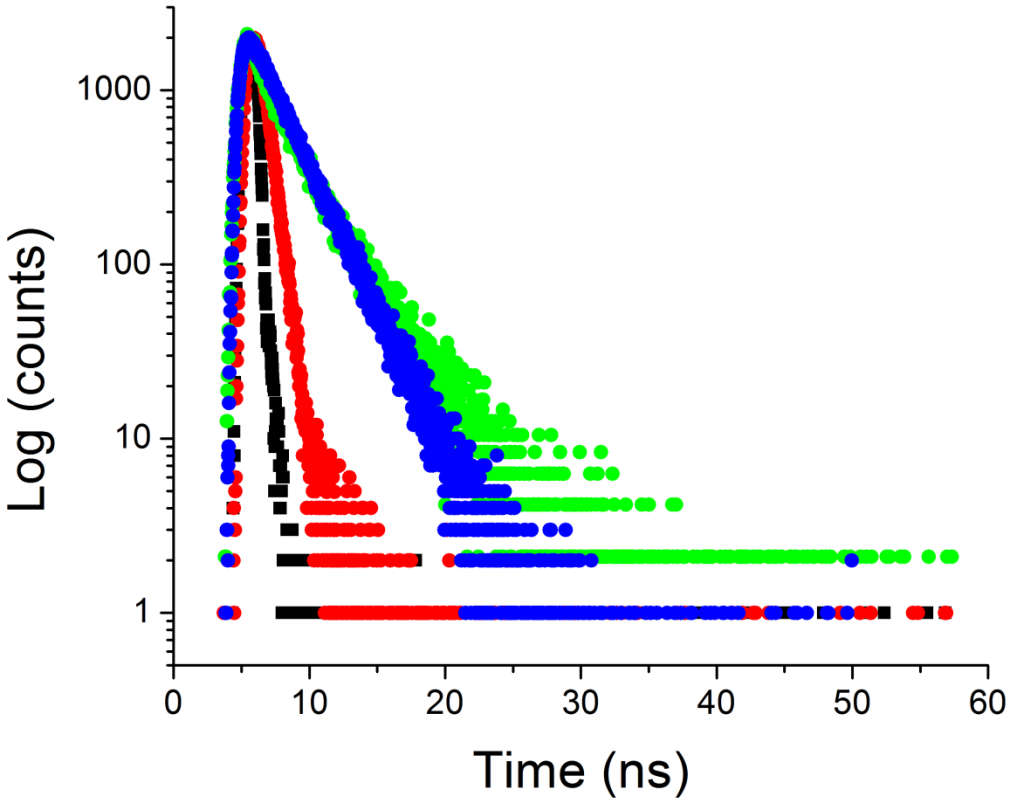

Log (counts)
1000
100
10
1
0
10
20
30
40
50
60
Time (ns)

Fig. S6. Life time decay profile of HL (●●●), HL-Zn^{2+} (●●●) and HL-HSO_4^- (●●●) ($\lambda_{excitation}$ = 370 nm)

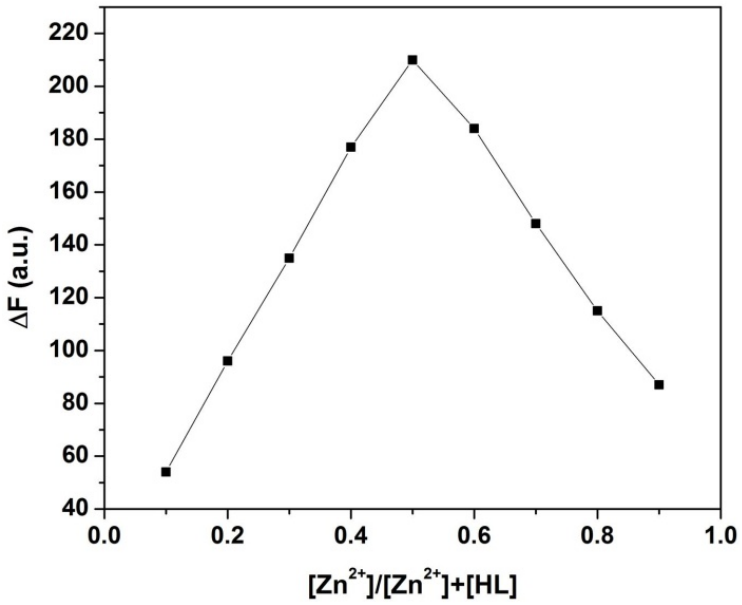


Fig. S7. Job's plot diagram of the receptor (HL) for Zn^{2+} (where ΔF indicates the change of emission intensity at 457 nm)

Determination of detection limit:

The detection limit was calculated based on the fluorescence titration. To determine the S/N ratio, the emission intensity of HL without any analyte was measured by 10 times and the standard deviation of blank measurements was found to be 5.0859×10^{-4}.

The limit of detection (LOD) of HL for Zn^{2+} was determined from the following equation: LOD = K × σ Where K = 3 in this case and σ = $(Sb_1)/(S)$; Sb_1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

From the graph we get slope = 23.3248, and Sb_1 value is 5.0859×10^{-4} (Fig. S8). Thus using the formula we get the LOD = 6.5×10^{-5} M.

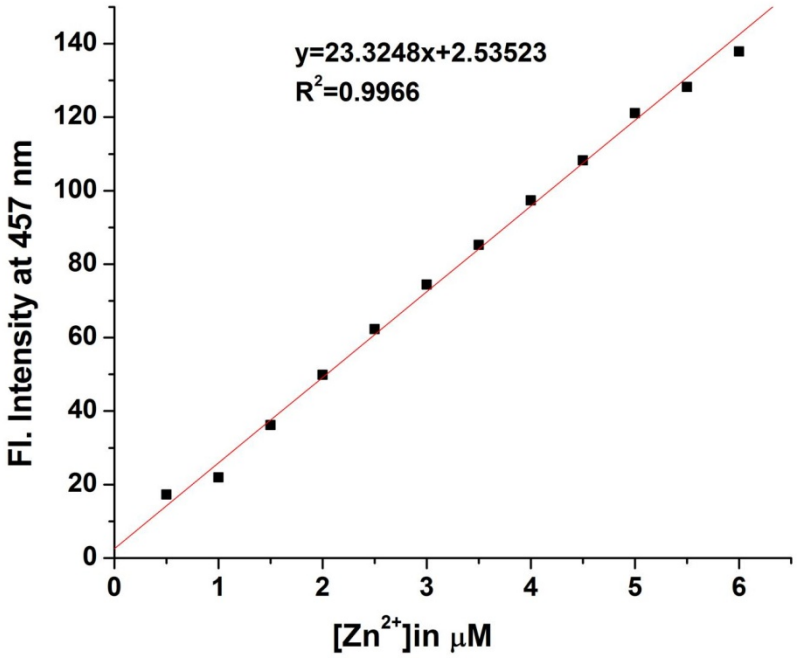


Fig. S8. Linear response curve of HL at 457 nm depending on the Zn^{2+} concentration.

Determination of binding constant from Fluorescence titration data:

Binding constant was calculated according equation. The binding constant β was calculated following the equation stated below.

$$\text{Log } (F-F_{min})/(F_{max}-F) = n\log [M^{n+}] + B$$

Here F_{min}, F and F_{max} indicate the emission intensity in absence of, at intermediate and at infinite concentration of metal ion respectively. $B = \log\beta$, where β is the total binding constant and n is the number of Zn^{2+} bind per ligand. From the plot n = 1.103 indicating 1:1 stoichiometry for the formed HL-Zn^{2+} complex (Fig. S8). From the intercept β is found to be 4.8×10^5.

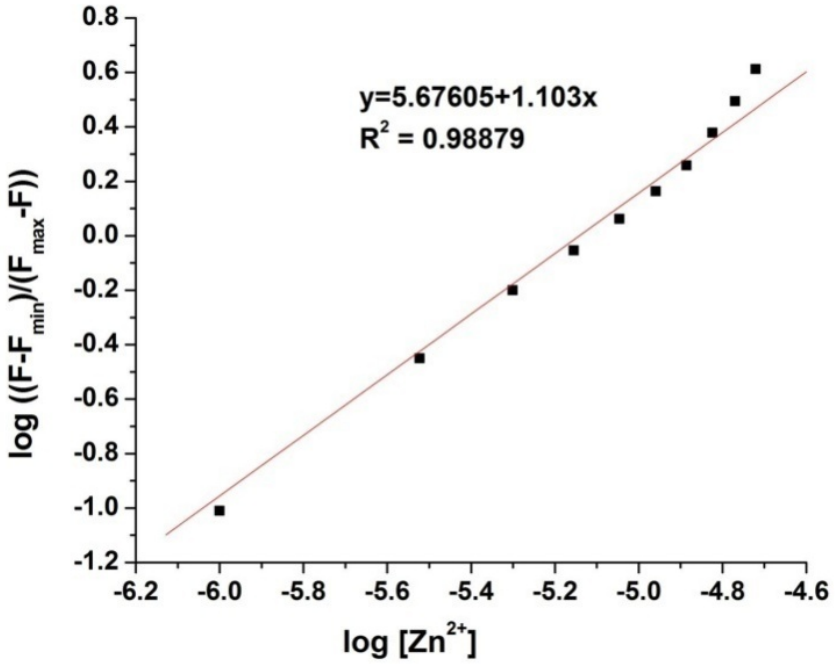


Fig. S9. Determination of binding constant of HL for Zn^{2+} from fluorescent titration data

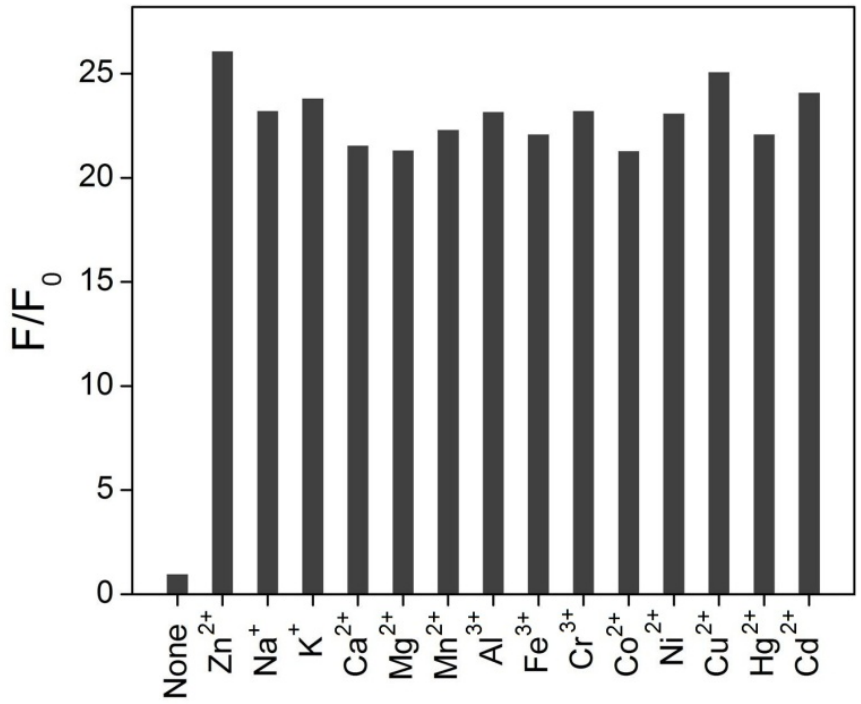


Fig. S10. Change in emission intensity of chemosensor (HL) upon addition of 1 equivalent of Zn^{2+} along with 2 equivalents of other metal ions to the receptor HL

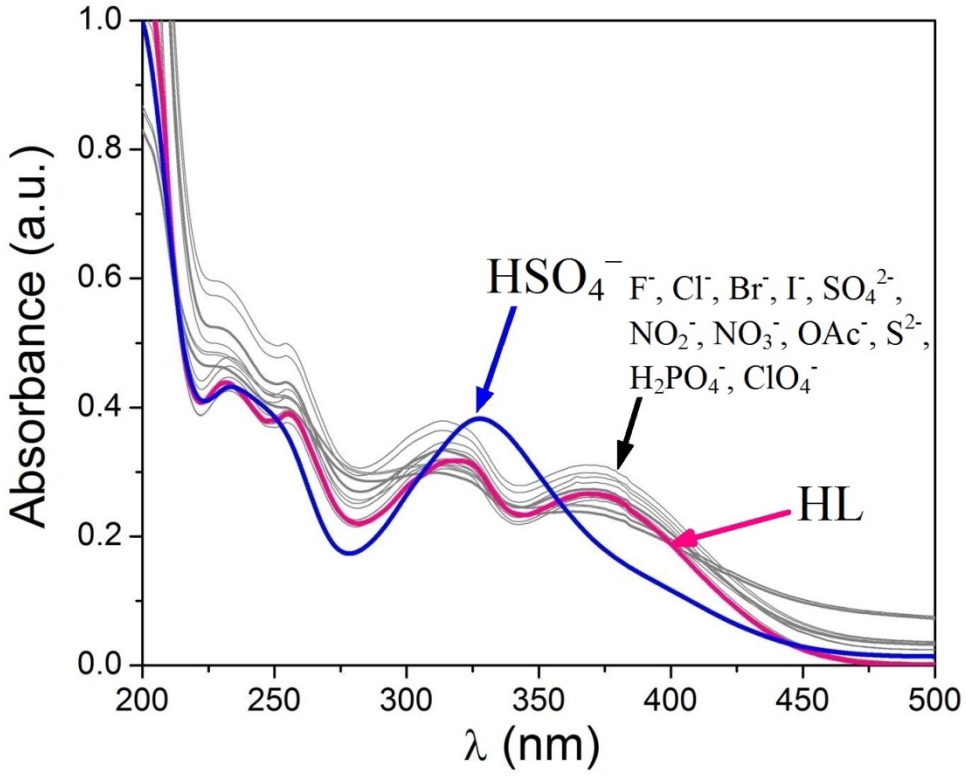


Fig. S11. UV-Vis spectra of chemosensor (HL) (10 μM) upon addition of 2 equivalent of various anions (100 μM).

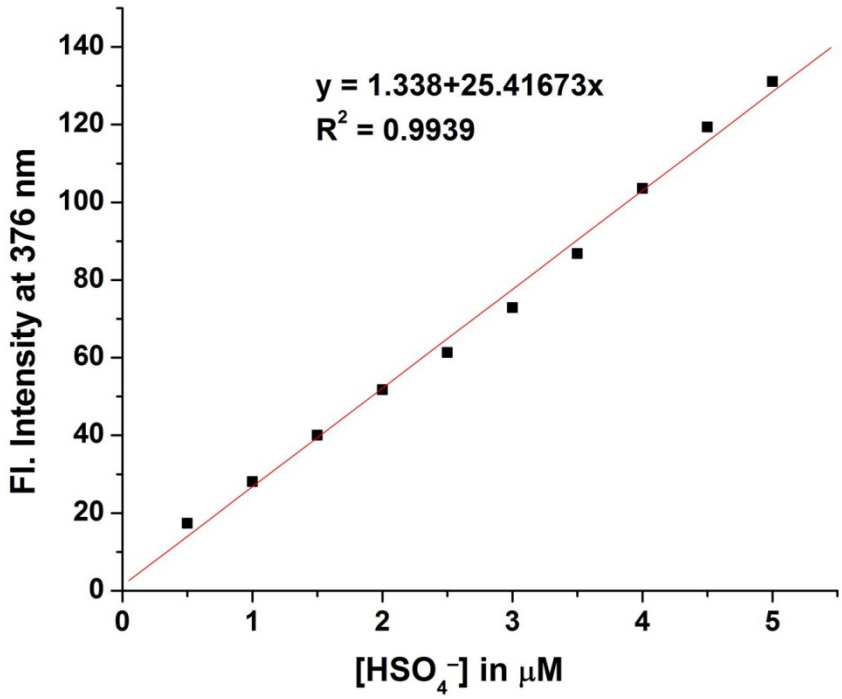


Fig. S12. Linear response curve of HL at 376 nm depending on the HSO_4^- concentration.

(From the graph we get slope = 25.41673, and Sb_1 value is 5.0859×10^{-4} .Thus using the formula we get the LOD = 0.274×10^{-6} M)

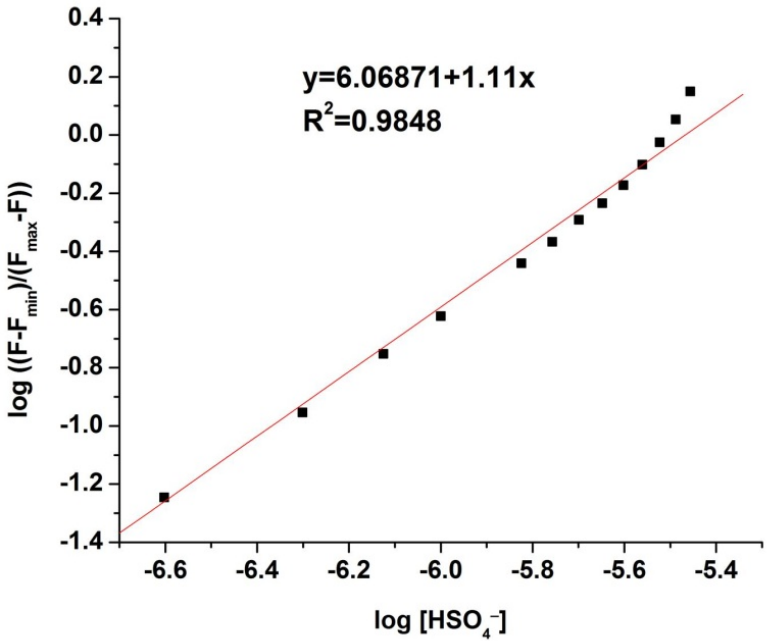


Fig. S13. Determination of binding constant of HL for HSO_4^- from fluorescent titration data

(For determination of binding constant of HSO_4^- with the chemosensor, β is found to be 1.17×10^6 and n = 1.11 indicating 1:1 stoichiometry for the formed HL-HSO_4^- complex)

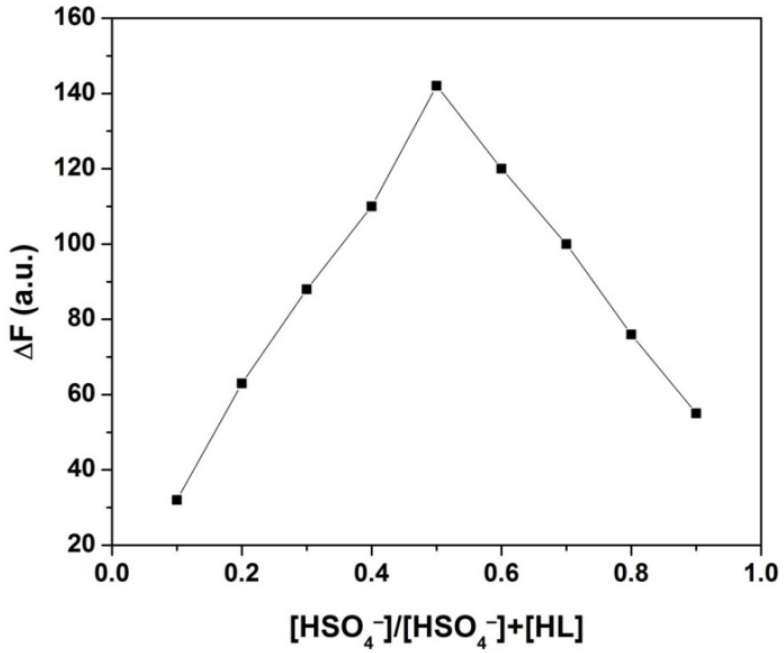


Fig. S14. Job's plot diagram of receptor for HSO_4^- (where ΔF indicates the change of emission intensity at 376 nm).

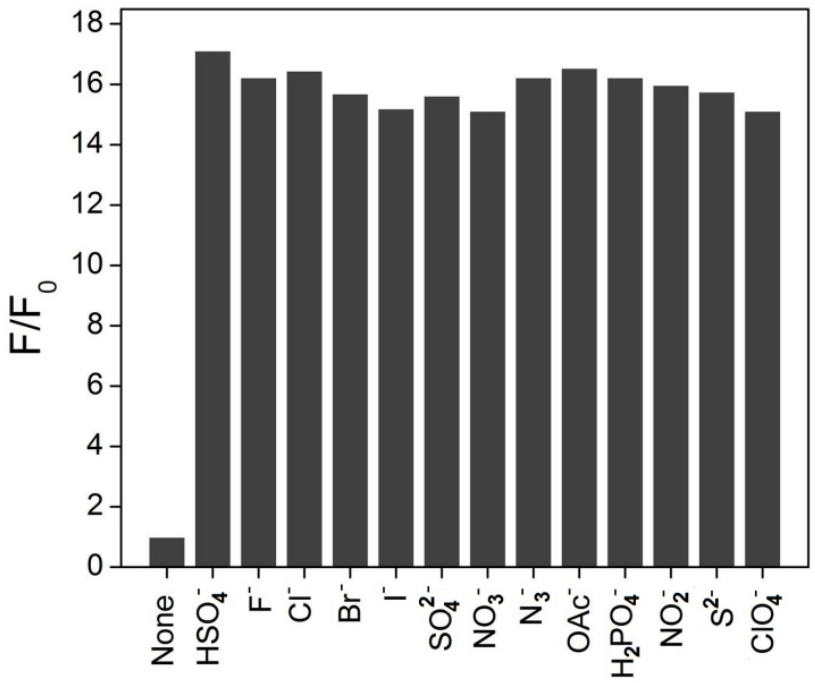
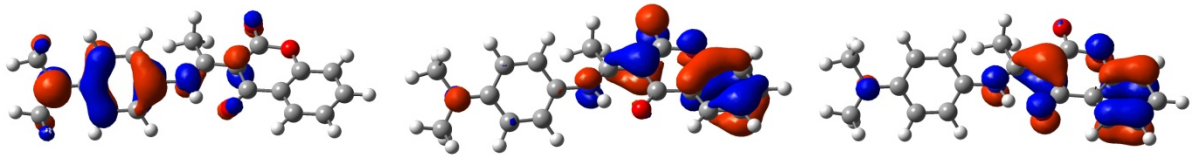


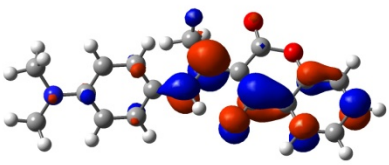
Fig. S15. Change in emission intensity upon addition of 1 equivalents of HSO_4^- along with 2 equivalents of other anions to the receptor HL

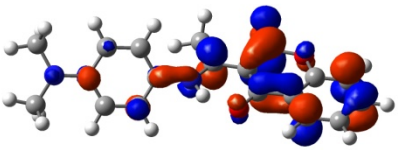


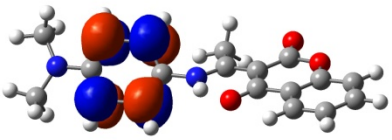
HOMO (E = -5.33 eV)

HOMO-1 (E = -6.19 eV)

HOMO-2 (E = -6.35 eV)

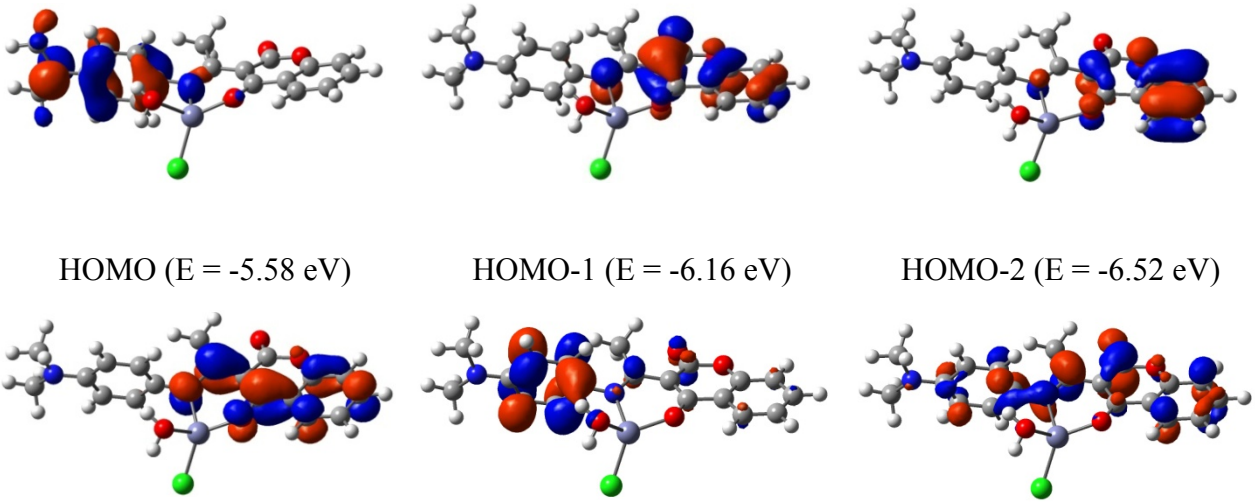






LUMO (E = -1.58 eV) LUMO+1 (E = -0.46 eV) LUMO+2 (E = -0.30 eV)

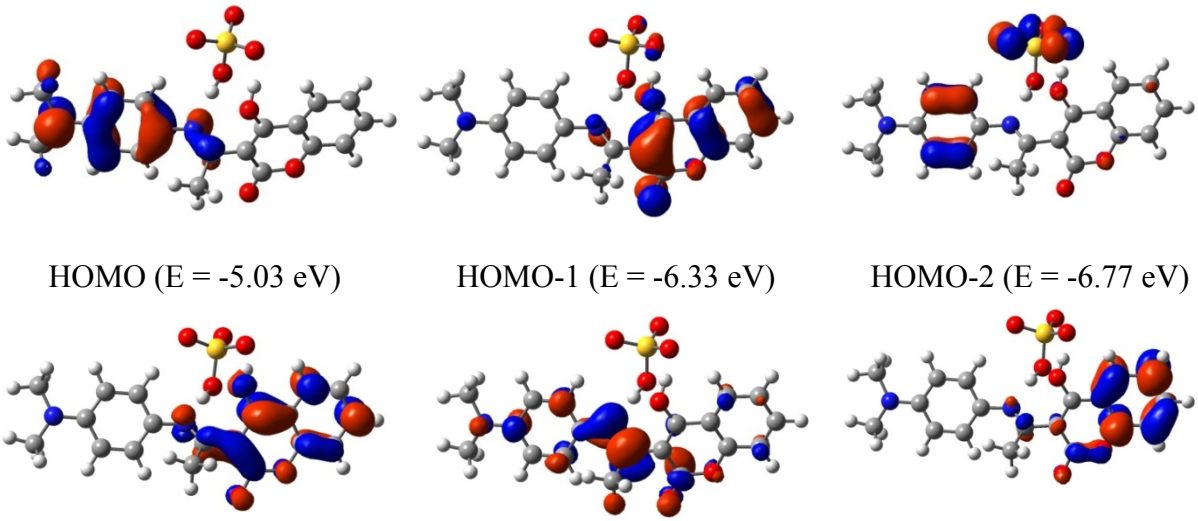
Fig. S16. Contour plots of selected molecular orbitals of chemosensor (HL)



HOMO (E = -5.58 eV) HOMO-1 (E = -6.16 eV) HOMO-2 (E = -6.52 eV)

LUMO (E = -1.75 eV) LUMO+1 (E = -0.76 eV) LUMO+2 (E = -0.48 eV)

Fig. S17. Contour plots of selected molecular orbitals of HL-Zn^{2+}



HOMO (E = -5.03 eV) HOMO-1 (E = -6.33 eV) HOMO-2 (E = -6.77 eV)

LUMO (E = -1.72 eV) LUMO+1 (E = -0.81 eV) LUMO+2 (E = -0.24 eV)

Fig. S18. Contour plots of selected molecular orbitals of HL-HSO_4^-