

Electronic Supplementary Material

**A turn-on fluorescent sensor for relay recognition of two
ions: From F⁻-selective sensor to highly Zn²⁺-selective
sensor by tuning electronic effects**

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Contents

1. General Methods	3
2. Synthesis of sensor molecule L2	4
3. Absorbance spectra of L2 in DMSO in the presence of fluoride anions	5
4. Plot of fluorescence intensity depending on the concentration of zinc ions	6
5. Determination of Detection Limit	7
6. The UV-vis spectroscopy and fluorescence spectroscopy for the stability and reproducibility of the sensor L2	8
7. IR spectra of sensor L2 and after adding fluoride anions	9
8. IR spectra of L2-F and after adding zinc ions	10
9. The Job's plot examined between zinc ions and L2-F	11
10. ESI/MS of L2	12
11. ESI/MS of L2-F with zinc	13
12. ¹ H-NMR spectrum of L2	14
13. ¹³ C-NMR spectrum of L2	15

1. General Methods

Fresh double distilled water was used throughout the experiment. All other reagents and solvents were commercially available at analytical grade and were used without further purification. ^1H -NMR and ^{13}C -NMR spectra were recorded on an Agilent DD2 at 600 MHz spectra. ^1H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. UV-visible spectra were recorded on a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were performed on a Shimadzu RF-5301 fluorescence spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer.

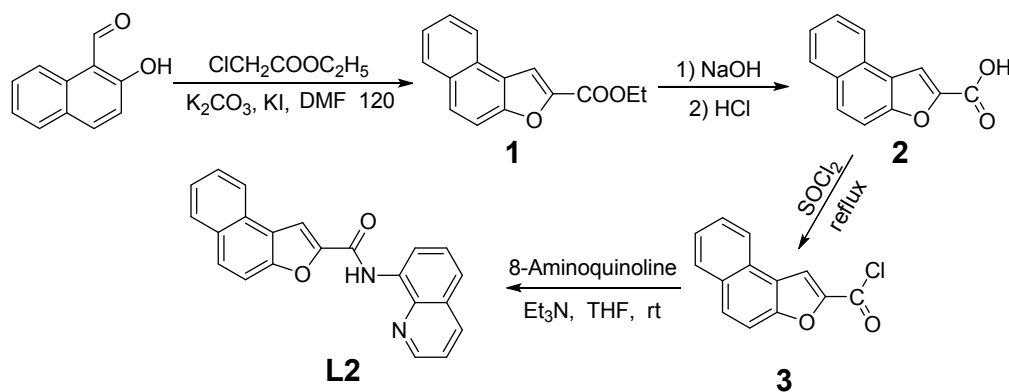
All the UV-vis experiments were carried out in DMSO on a Shimadzu UV-2550 spectrometer. Any changes in the UV-vis spectra of the synthesized compound were recorded on addition of perchlorate salts while keeping the ligand concentration constant (2.0×10^{-5} M) in all experiments. perchlorate salt (4.0×10^{-4} M) of anions (Fe^{3+} , Hg^{2+} , Ag^+ , Ca^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , Cr^{3+} , and Mg^{2+}) and Tetrabutylammonium salt (1.0×10^{-3} M) of anions (F^- , Cl^- , Br^- , I^- , AcO^- , H_2PO_4^- , HSO_4^- and ClO_4^-) and sodium salt (1.0×10^{-3} M) of anions (CN^-) were used for the UV-vis experiments.

All the fluorescence spectroscopy was carried out in DMSO on a Shimadzu RF-5301 spectrometer. Any changes in the fluorescence spectra of the synthesized compound were recorded on addition of perchlorate salts while keeping the ligand concentration constant (2.0×10^{-5} M) in all experiments. perchlorate salt (4.0×10^{-4} M) of anions (Fe^{3+} , Hg^{2+} , Ag^+ , Ca^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , Cr^{3+} , and Mg^{2+}) and Tetrabutylammonium salt (1.0×10^{-3} M) of anions (F^- , Cl^- , Br^- , I^- , AcO^- , H_2PO_4^- , HSO_4^- and ClO_4^-) and sodium salt (1.0×10^{-3} M) of anions (CN^-) were used for the fluorescence experiments

For $^1\text{H-NMR}$ titrations, the solution of **L2** was prepared in $\text{DMSO-}d_6$ and the appropriate concentrated solution of guest was prepared in $\text{DMSO-}d_6$. Aliquots of the two solutions were mixed directly in NMR tubes.

2. Synthesis of sensor molecule L2

Compound **L2** can be readily prepared by a simple and low-cost amide reaction of naphtha [2, 1-*b*] furan-2-carbonyl chloride and 8-aminoquinoline (Scheme S1). naphtha [2, 1-*b*] furan-2-carbonyl chloride (0.462 g, 2 mmol), 8-aminoquinoline (0.360 g, 2.5 mmol) and 2.5ml triethylamine (Et_3N) were combined in hot absolute tetrahydrofuran (30 mL). The solution was stirred under reflux for 6 hours. After cooling to room temperature, the yellow precipitate was filtered, washed three times with hot absolute tetrahydrofuran, then recrystallized with THF to give a yellow powder product **L2** (1.56 mmol) in 78% (m. p. $>300\text{ }^\circ\text{C}$), IR: (KBr, cm^{-1}) ν : 3338 ($-\text{NH}-$), 3118 ($\text{C}=\text{CH}$), 3046 (ArH), 1681 ($\text{C}=\text{O}$), 1596 ($\text{C}=\text{C}$), 1564 ($\text{C}=\text{N}$), 1531 ($\text{C}=\text{C}$), 1487 ($\text{C}-\text{N}$). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, 600 MHz): δ 10.94 (1H, s, NH), 9.08 (1H, s, $\text{C}=\text{CH}$), 8.94 (1H, d, ArH), 8.57–8.52 (3H, m, ArH), 8.14–8.04 (3H, m, ArH), 7.82–7.62(5H, m, ArH); $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$, 150 MHz): δ 155.85, 152.48, 149.32, 147.84, 137.62, 137.76, 133.40, 130.11, 128.88, 128.77, 127.81, 127.31, 127.03, 125.53, 123.88, 122.55, 122.46, 116.35, 112.58, 111.10, 109.67, 109.22; Anal. calcd for $\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_2$: C, 78.11, H, 4.14, N, 8.28, O, 9.47; found C, 78.07; H, 4.11; N, 8.33; O, 9.49.



Scheme S1 Synthesis of the sensor compound **L2**.

3. Absorbance spectra of L2 in DMSO in the presence of fluoride anions

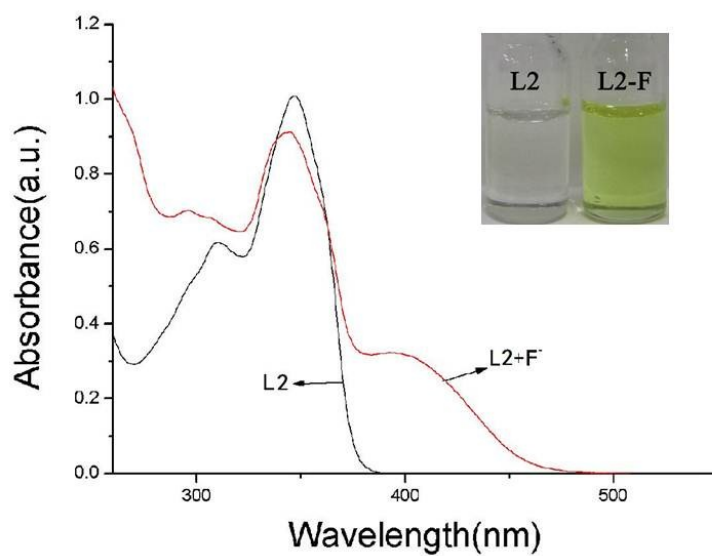


Fig. S1: Absorbance spectra of **L2** in DMSO in the presence of fluoride anions (20 equiv.). Inset: photograph showing the change in color of the solution of **L2** in DMSO after addition of fluoride anions (20 equiv.).

4. Plot of fluorescence intensity depending on the concentration of zinc ions

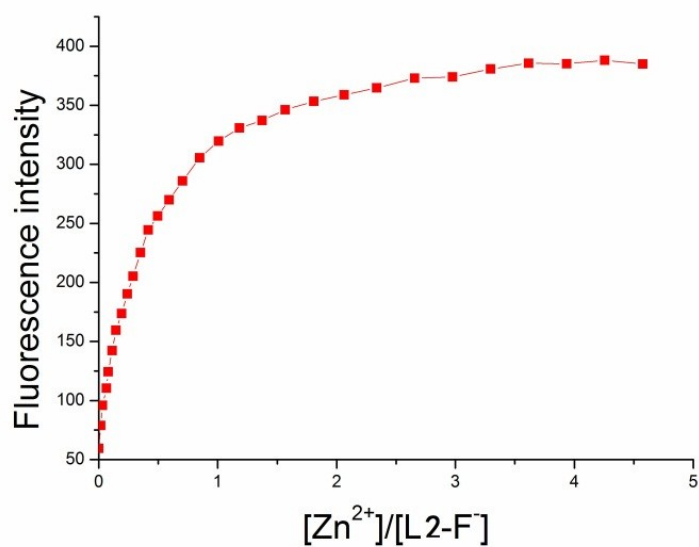
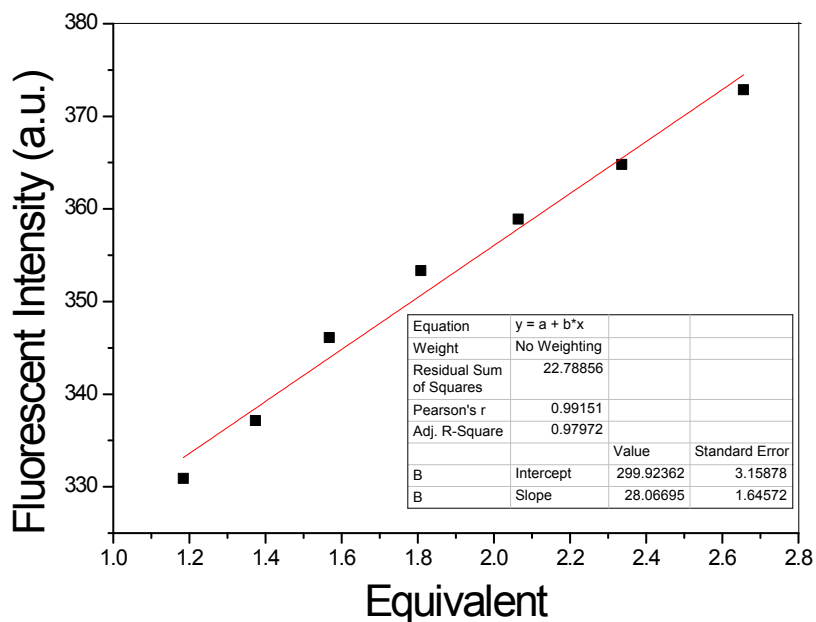


Fig. S2: A plot of fluorescence intensity depending on the concentration of zinc ions in the range from 0 to 5 equivalents in **L2-F**.

5. Determination of Detection Limit



Linear Equation: $Y = 28.0669 \times X + 299.9236$ $R = 0.979$

$$S = 2.8067 \times 10^7 \quad \delta = \sqrt{\frac{\sum(F - F)^2}{(N - 1)}} = 1.9647 (N = 15) \quad K$$

= 3

$$LOD = K \times \delta/S = 2.1 \times 10^{-7} \text{ M}$$

Fig. S3: The photograph of the fluorescent spectrum linear range.

6. The UV-vis spectroscopy and fluorescence spectroscopy for the stability and reproducibility of the sensor L2

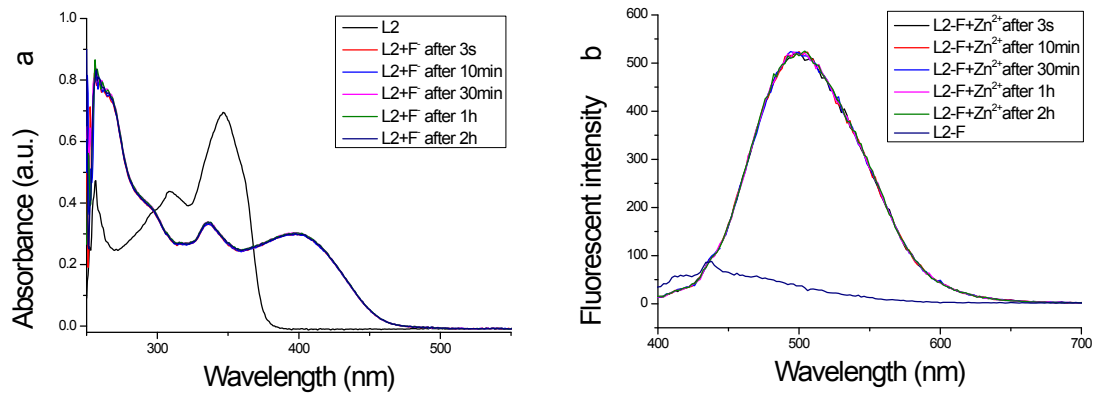


Fig. S4: The UV-vis spectroscopy and fluorescence spectroscopy for the stability and reproducibility of the sensor **L2**.

7. IR spectra of sensor L2 and after adding fluoride anions

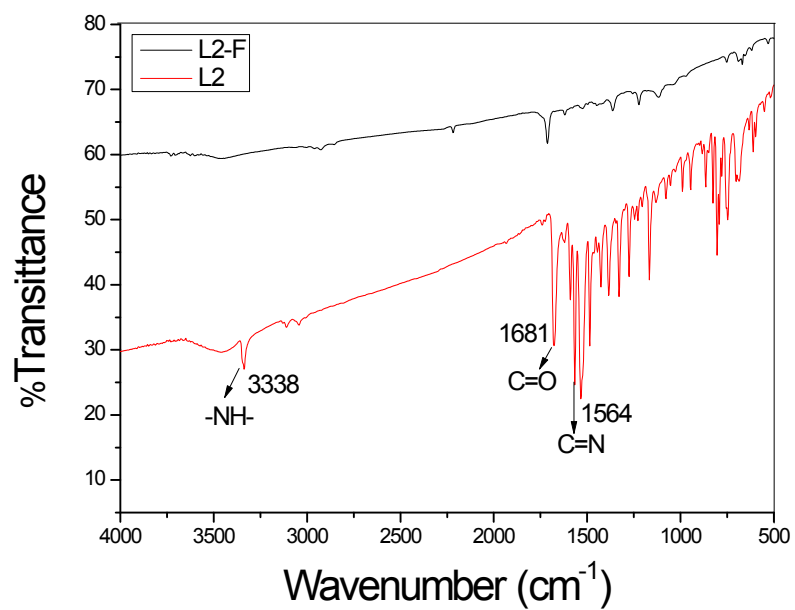


Fig. S5: IR spectra of sensor L2 and after adding fluoride anions in KBr disks.

8. IR spectra of L2-F and after adding zinc ions

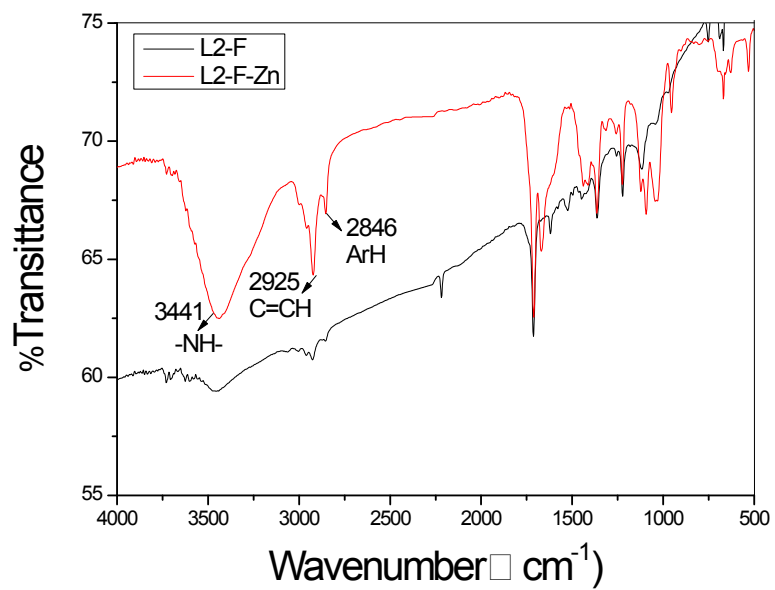


Fig. S6: IR spectra of L2-F and after adding zinc ions in KBr disks.

9. The Job's plot examined between zinc ions and L2-F

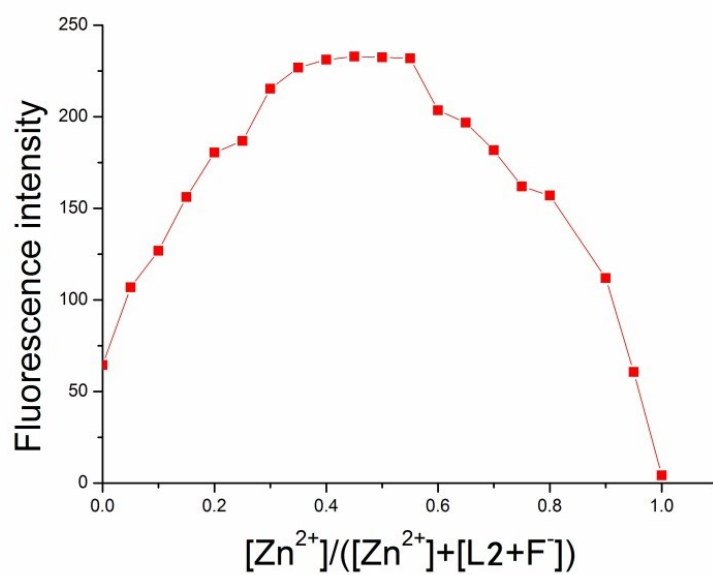


Fig. S7: The Job's plot examined between zinc ions and L2-F, indicating the 1:1 stoichiometry for L2-F and zinc ion.

10. ESI/MS of L2

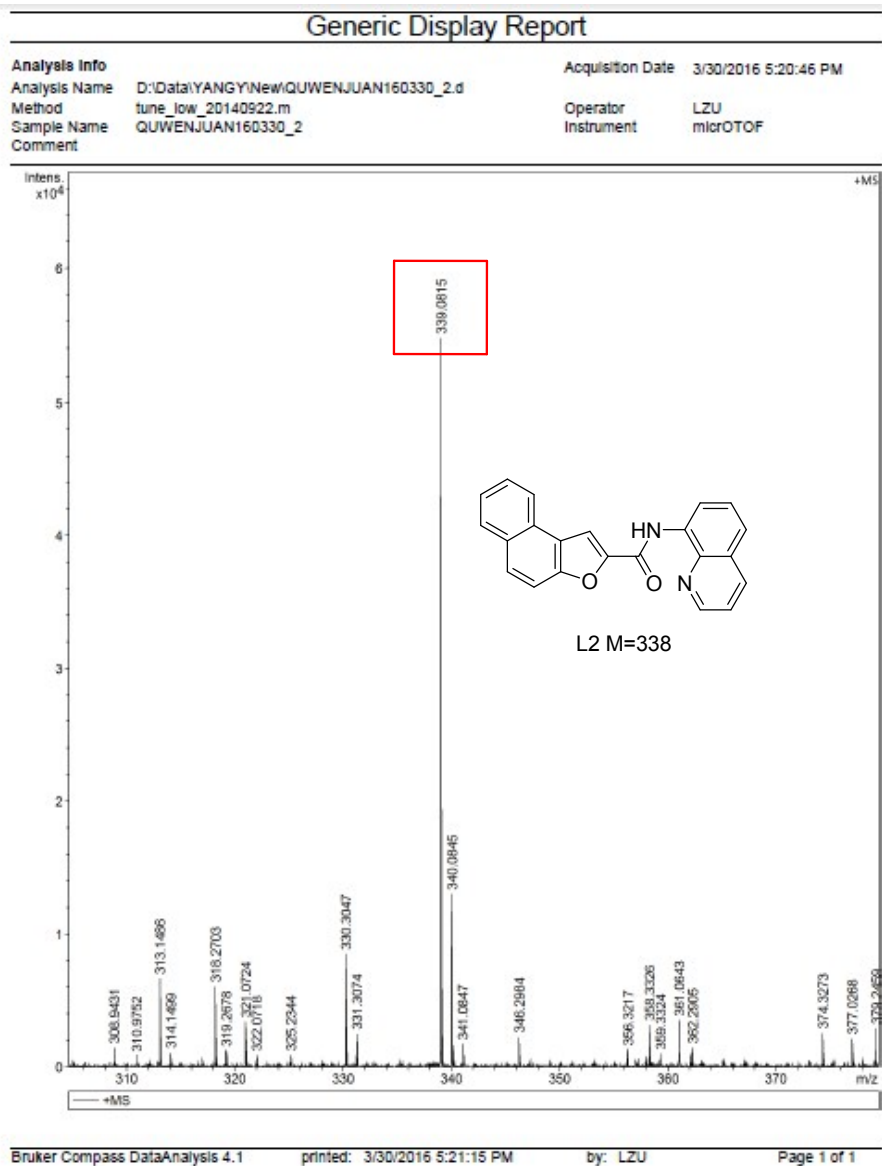


Fig. S8: The ESI/MS of L2 in DMSO.

11. ESI/MS of L2-F with zinc

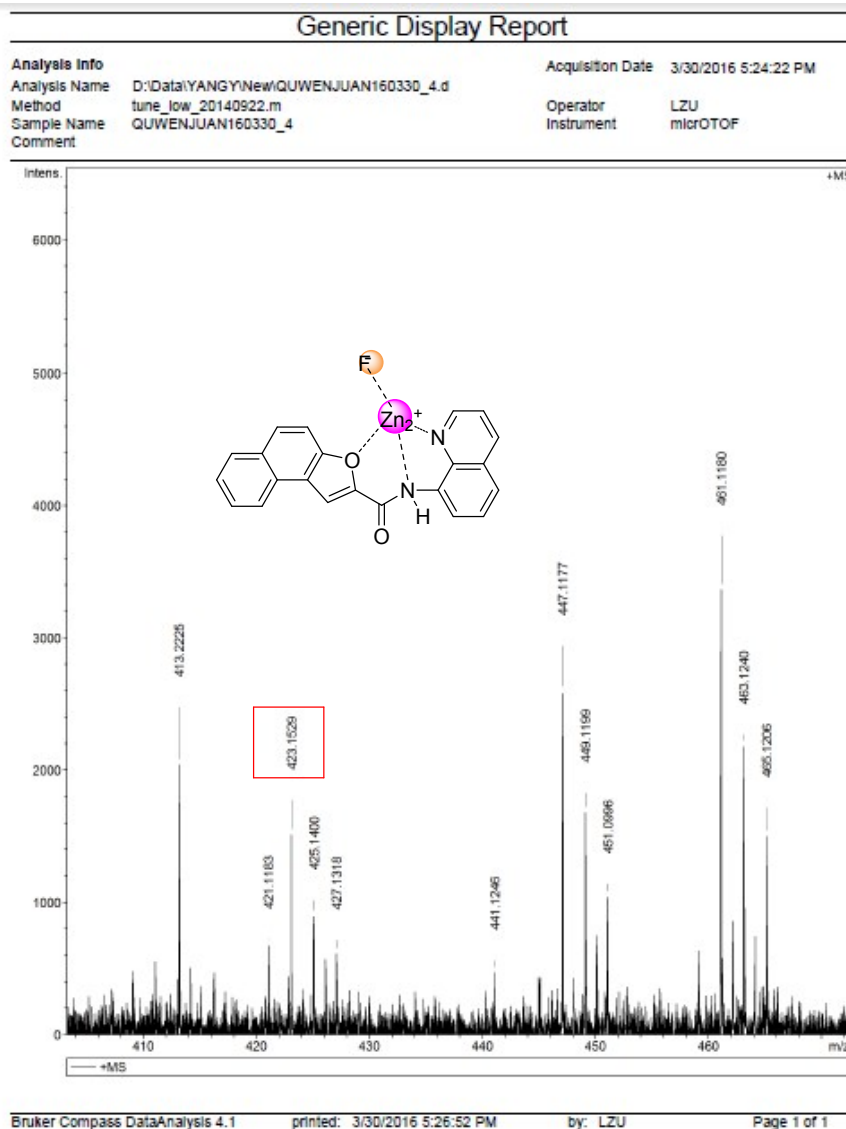


Fig. S9: The ESI/MS of L2-F with zinc in DMSO.

12. ^1H -NMR spectrum of L2

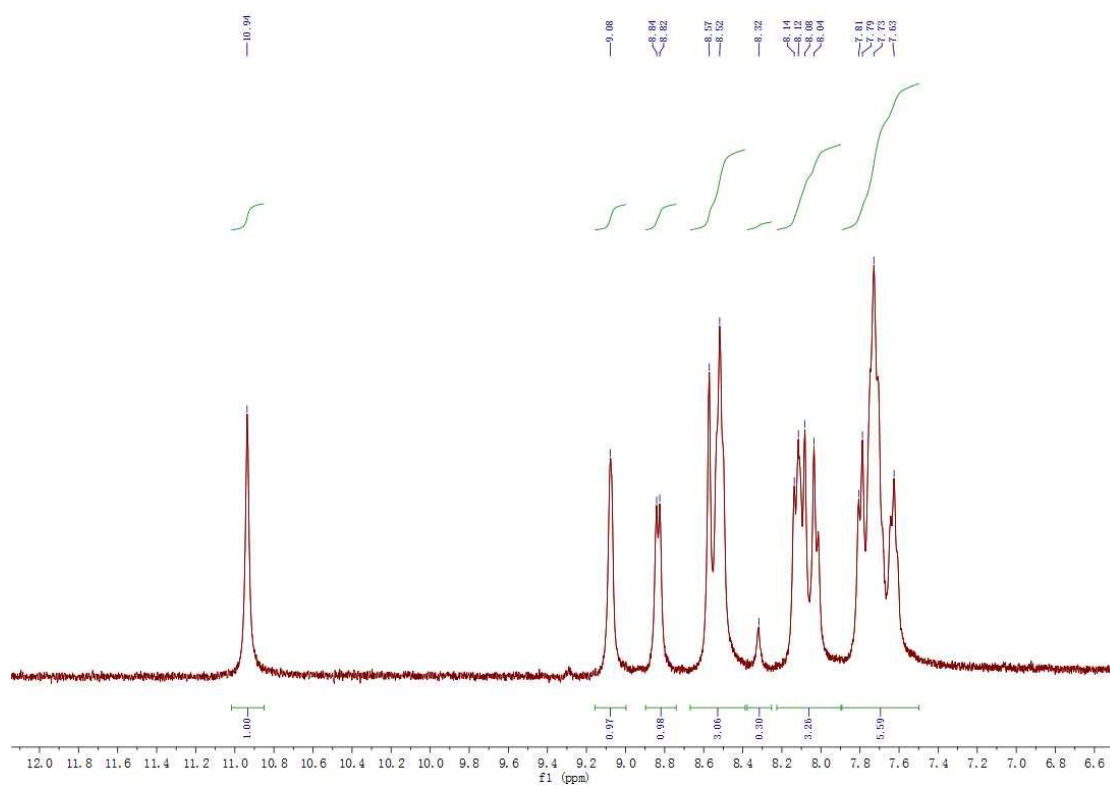


Fig. S10: ^1H -NMR spectrum of L2 in $\text{DMSO}-d_6$.

13. ^{13}C -NMR spectrum of L2

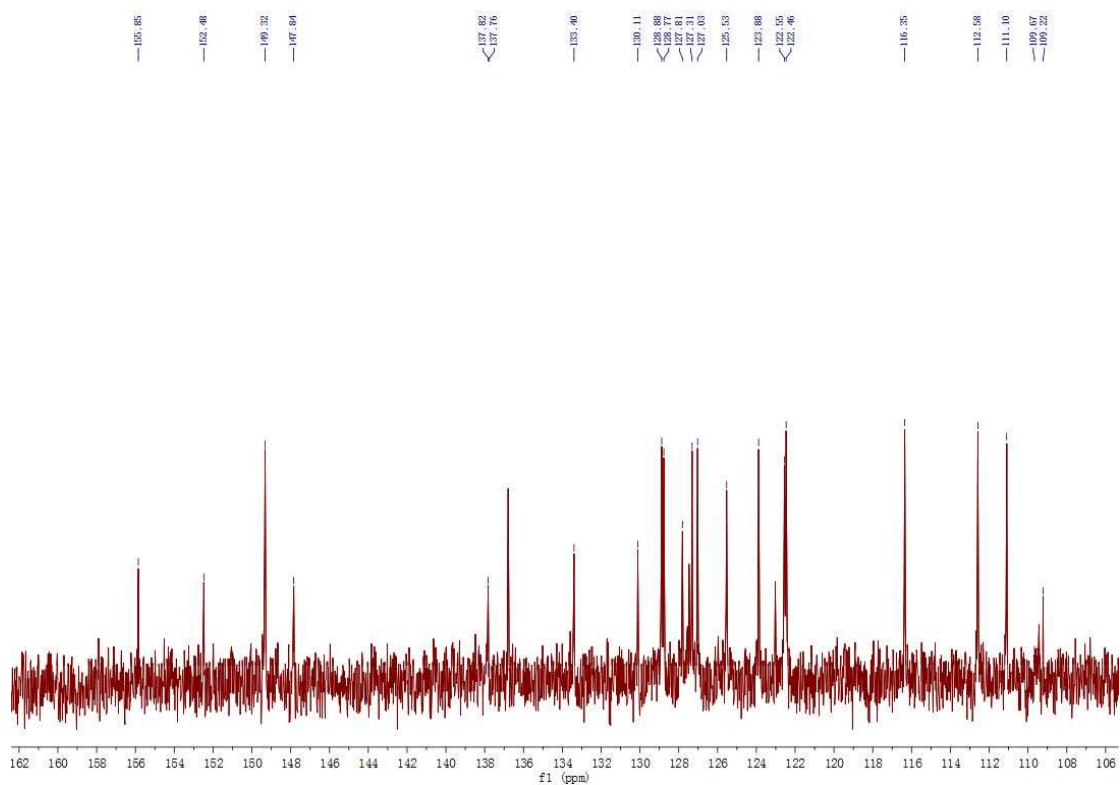


Fig. S11: ^{13}C -NMR spectrum of L2 in $\text{DMSO}-d_6$.