

Supporting Information

A New Chemosensor that Signals Hg(II), Cu(II) and Zn(II) at Different Emission Wavelengths: Selectivity toward Hg(II) in Acetonitrile

*B. Nisar Ahamed, I. Ravikumar and Pradyut Ghosh**

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,

2A & 2B Raja S. C. Mullick Road, Kolkata 700032, India

E-mail: icpg@iacs.res.in

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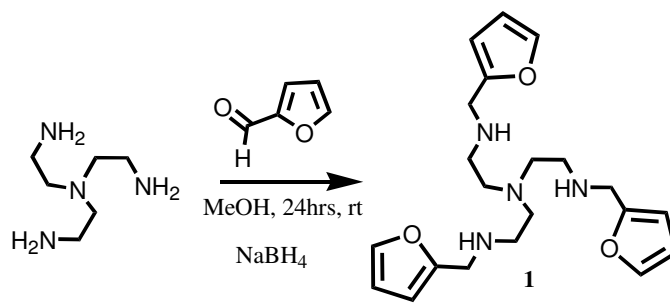
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Experimental Details.

Materials and Methods: Tris-(2-aminoethyl)amine (tren), 2-Chloromethylquinoline hydrochloride, 9-Hydroxymethyl anthracene, perchlorate salts of Cu(II), Zn(II), Cd(II), Hg(II), Li(I), Na(I), K(I), Ag(I), Ca(II) and nitrate salt of Ni(II) were purchased from Aldrich and were used directly without further purification. Furfuraldehyde, sodium borohydride, potassium carbonate, Phosphorus tribromide, chloroform, methanol, dichloromethane, acetonitrile, toluene and tetrahydrofuran were purchased from S.D. Fine Chemicals, India. Solvents were dried by conventional methods and distilled under N_2 atmosphere before being used. 9-Bromomethyl anthracene was synthesized as per literature procedure.¹ ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 MHz and 75

MHz FT-NMR spectrometers respectively using tetramethylsilane as an internal reference. MS measurements were carried out on a Qtof Micro YA263 HRMS instrument. The absorption spectra were recorded with a Perkin Elmer Lambda 950 UV-VIS-NIR scanning spectrophotometer at 298 K. The fluorescence spectra were recorded using Perkin Elmer LS-55 luminescence spectrophotometer at room temperature. CAUTION: *Perchlorate salts of metal complexes with organic ligands are potentially explosive. All due precautions should be taken.*

Synthesis of 1:

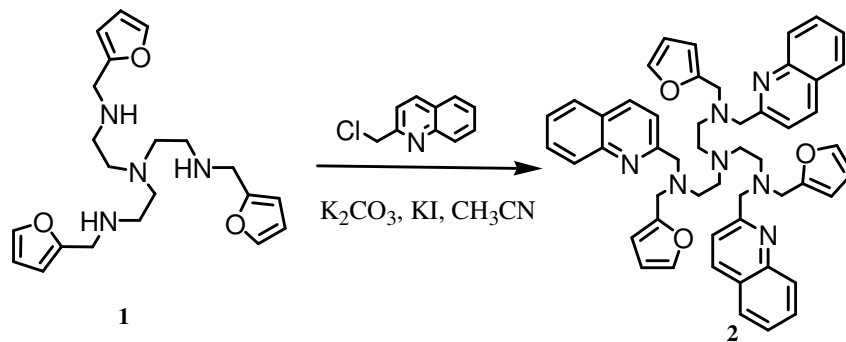


Scheme 1. Synthesis of **1**

A dry methanolic solution (50 ml) of Tris-(2-aminoethyl)amine (tren), (0.45 ml, 3 mmol) was added slowly to a stirred solution of furfuraldehyde (0.75 ml, 9 mmol) in dry methanol (75 ml) and the stirring was continued for 24 hours at room temperature under nitrogen atmosphere. After this period, excess of NaBH₄ was added in portions to the stirring solution in ice cold condition; resulting

solution was stirred for 8 hours at room temperature and then refluxed for another 2 hours, the reaction mixture was cooled to rt, the solvent was removed under vacuum and the residue was dissolved in CHCl_3 and was washed with water (3 x 100 ml), dried over anhydrous Na_2SO_4 and evaporated under vacuum to give dark yellowish-brown oil, which was purified by silica gel (stationary phase) column chromatography using Hexane-EtOAc gradient as eluent to afford **1**. Yield: 856.00 mg (74%), Calculated for $\text{C}_{21}\text{H}_{30}\text{N}_4\text{O}_3$: $[\text{M}+\text{H}]^+$ $m/z = 386.4879$, Found: 387.3949; $^1\text{H-NMR}$ δ (CDCl_3 , 300 MHz, ppm): 7.33 (s, 3H, Ar-H), 6.29 (s, 3H, Ar-H), 6.17 (s, 3H, Ar-H), 3.75 (s, 6H, ArCH_2), 2.83 (b, 3H, N-H), 2.64(t, 6H, $\text{ArCH}_2\text{NCH}_2$, $J = 5.01\text{Hz}$), 2.56 (t, 6H, $\text{ArCH}_2\text{NCH}_2\text{CH}_2\text{N}$, $J = 5.1\text{ Hz}$). ^{13}C NMR (CDCl_3 , 75MHz, ppm): δ 45.87, 46.6, 107.11, 108.70, 110.15, 141.79, 153.54.

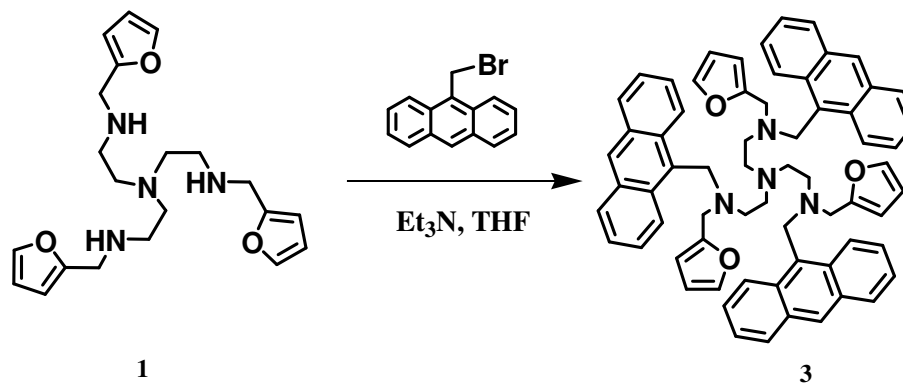
Synthesis of 2:



Scheme 2. Synthesis of **2**

The ligand **1** (0.500 g, 0.6 mmol) was dissolved in dry CH₃CN (75 ml) and anhydrous K₂CO₃ (0.256 g, 1.85 mmol) was added. This suspension was stirred for half an hour at 60°C. To the stirring solution 2-Chloromethylquinoline (0.395g, 1.85 mmol) was added and the mixture was stirred for another 3 hours in presence of catalytic amount of KI. Stirring and refluxing were continued for 24 hrs and then the reaction mixture was allowed to cool to rt. The excess K₂CO₃ was filtered off and washed with CH₃CN. Combine filtrates were collected in a round bottom flask and solvent was removed under vacuum and dissolved in CHCl₃. The chloroform suspension was washed with distilled water (3 x 100 ml). The organic layers were collected and dried over anhydrous Na₂SO₄ and evaporated to dryness to give a crude product of blackish-yellow semi solid of **2**. This crude product was further purified by silica gel (stationary phase) column chromatography using CHCl₃-EtOAc gradient as eluent to afford **2**. Yield 155 mg (32%). Calculated for C₅₁H₅₁N₇O₃: [M+H peak]⁺ m/z = 809.99, Found: 810.2151; ¹H NMR δ (CDCl₃, 600 MHz), 8.02 (d, 3H, Ar-H), 7.98 (d, 3H, Ar-H), 7.71 (d, 3H, Ar-H), 7.64 (t, 3H, Ar-H), 7.55 (d, 3H, Ar-H), 7.44 (t, 3H, Ar-H), 7.29 (d, 3H, Ar-H), 6.22 (d, 3H, Ar-H), 6.12 (d, 3H, Ar-H), 3.85 (s, 6H, ArCH₂), 3.61 (s, 6H, Ar-H), 2.60 (t, 6H, ArCH₂NCH₂, J = 5.01 Hz), 2.57 (t, 6H, ArCH₂NCH₂CH₂N, J = 5.1 Hz). ¹³C NMR (CDCl₃, 75 MHz, ppm) δ 50.54, 50.81, 50.82, 108.92, 110.05, 120.05, 120.98, 126.0, 126.32, 127.23, 127.44, 128.49, 128.76, 129.28, 129.49, 136.29, 141.92, 142.23, 147.35, 151.88, 160.18.

Synthesis of 3:



Scheme 3. Synthesis of **3**

The Ligand **1** (0.500 g, 0.6 mmol) was dissolved in dry THF (60 mL), anhydrous Et₃N (0.246 g, 2.4 mmol) was added and the mixture was stirred for an hour at room temperature under nitrogen atmosphere. Freshly prepared 9-Bromomethylanthracene¹ (0.515 g, 19 mmol) was added and the reaction mixture was stirred and refluxed for two-days and allowed to cool to rt, the solvent were removed under vacuum and the residue was extracted with CHCl₃. The combined organic layers were dried over anhydrous Na₂SO₄, evaporated to dryness, washed with diethyl ether, giving a yellowish semi-solid which was purified by Alumina (stationary phase) column chromatography using CHCl₃-CH₃OH gradient as eluent to afford **3**. Yield: 212.5 mg (37%). Calculated for C₆₆H₆₀N₄O₃: [M+H peak]⁺ *m/z* = 809.99, Found: 810.2151; ¹H NMR δ (CDCl₃, 300 MHz, ppm), 8.31 (d, 2H, Ar-H), 8.22 (d, 3H, Ar-H), 7.35 (m,

7H, Ar-H), 6.25 (s, 3H, Ar-H), 5.99 (s, 3H, Ar-H), 4.147(S, 2H, ArCH₂), 3.35 (s, 2H, ArCH₂), 2.28 (t, 2H, ArCH₂NCH₂CH₂N), 2.12 (t, 2-H, ArCH₂NCH₂CH₂N). ¹³C NMR(CDCl₃, 75MHz, ppm) δ 50.49, 51.48, 52.61, 60.85, 109.07, 110.67, 121.23, 127.37, 128.18, 128.93, 129.79, 136.55, 142.73, 147.36, 152.55, 160.68.

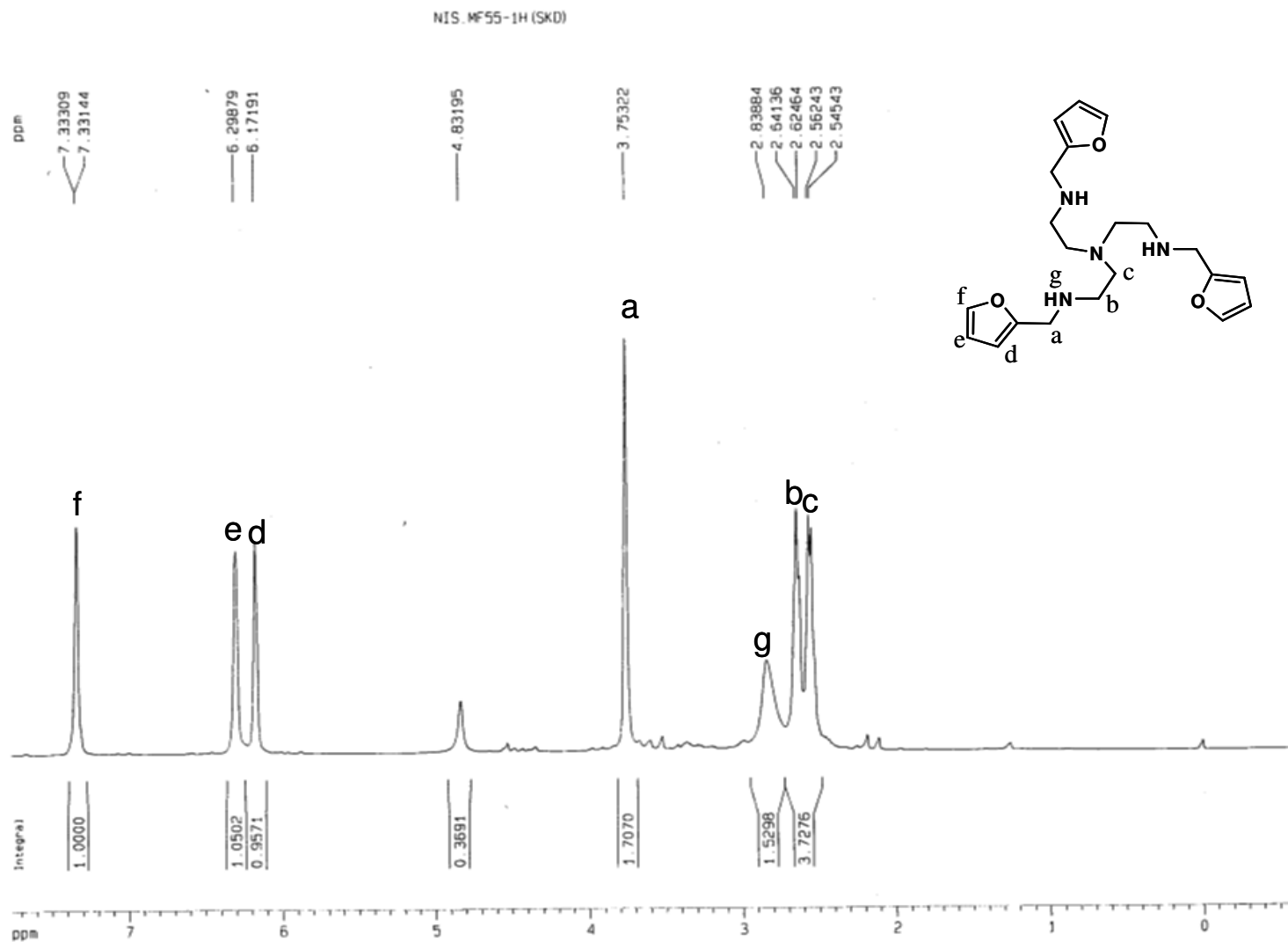


Figure S1. ^1H NMR spectrum of **1** in CDCl_3

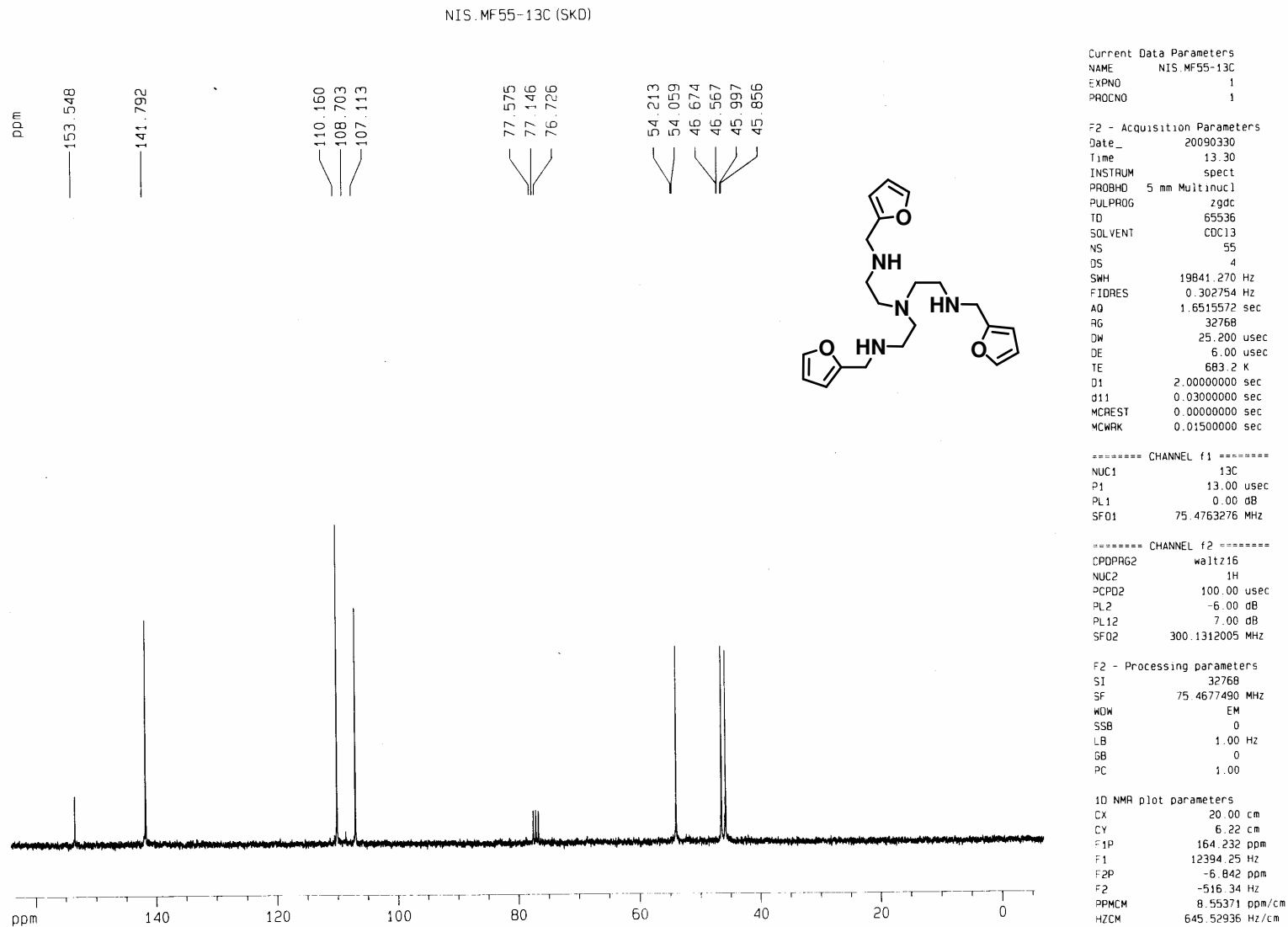


Figure S2. ¹³C NMR spectrum of 1 in CDCl₃

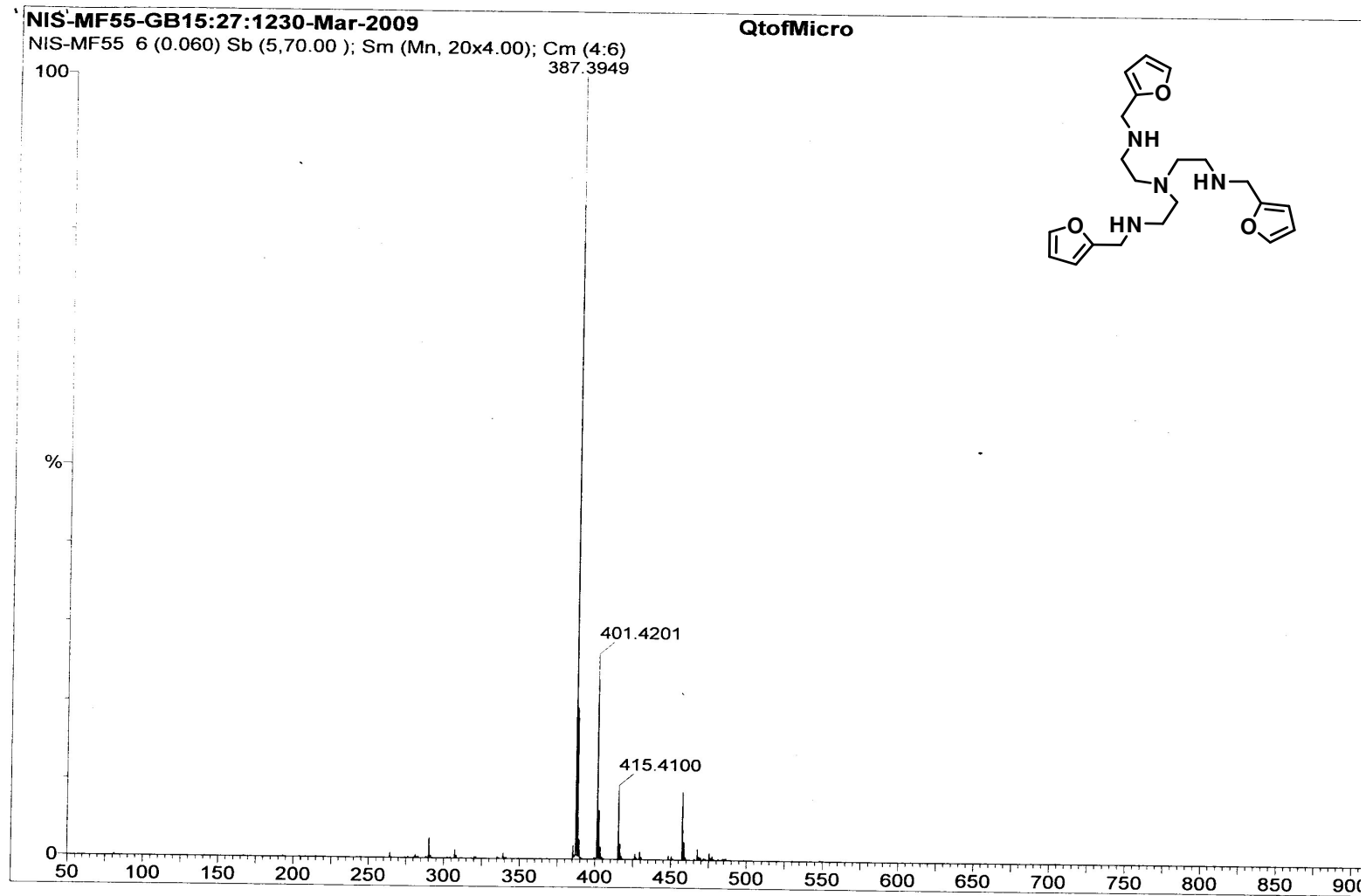


Figure S3. HRMS spectrum of **1**

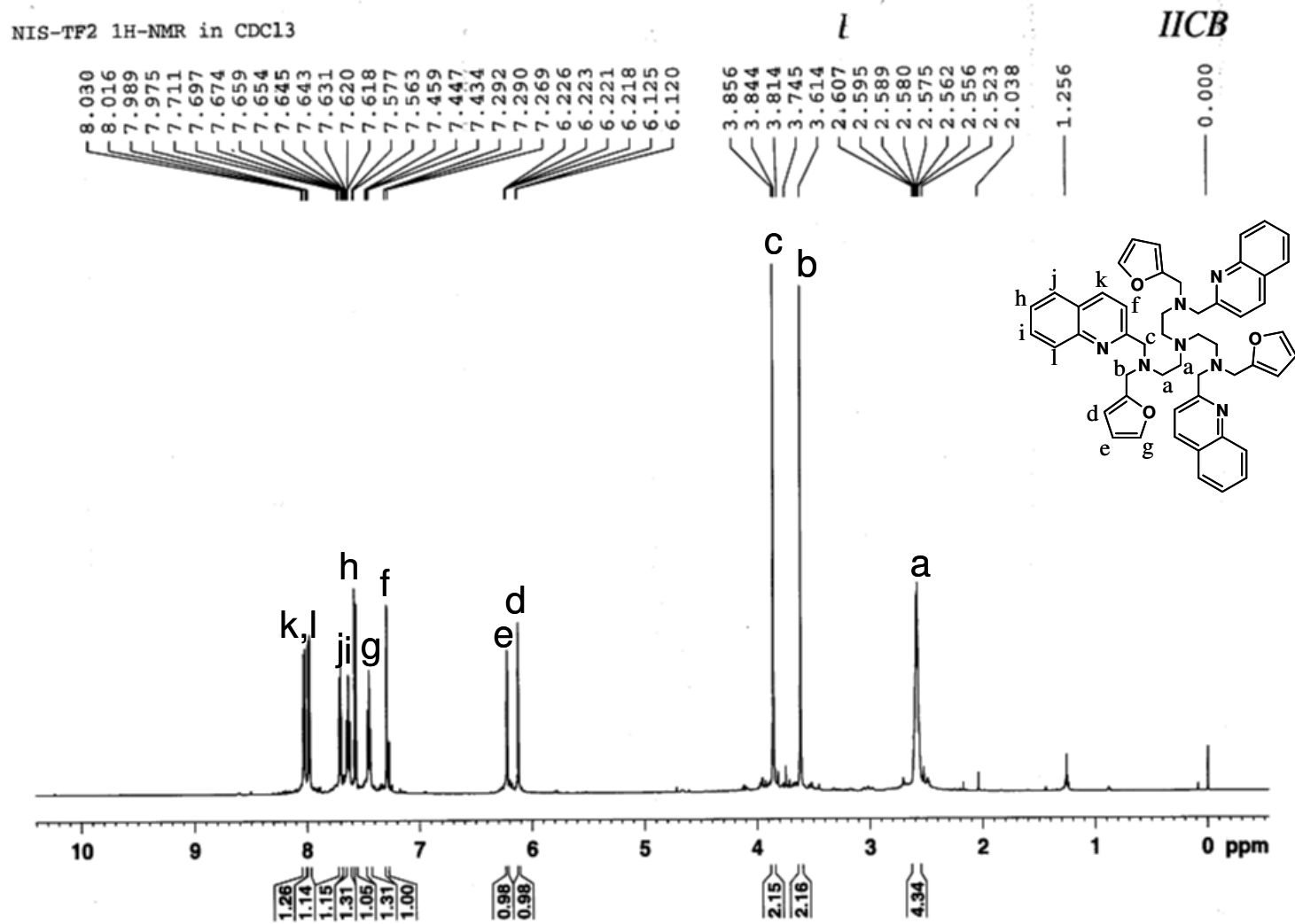


Figure S4. ¹H NMR Spectrum of 2 in CDCl₃

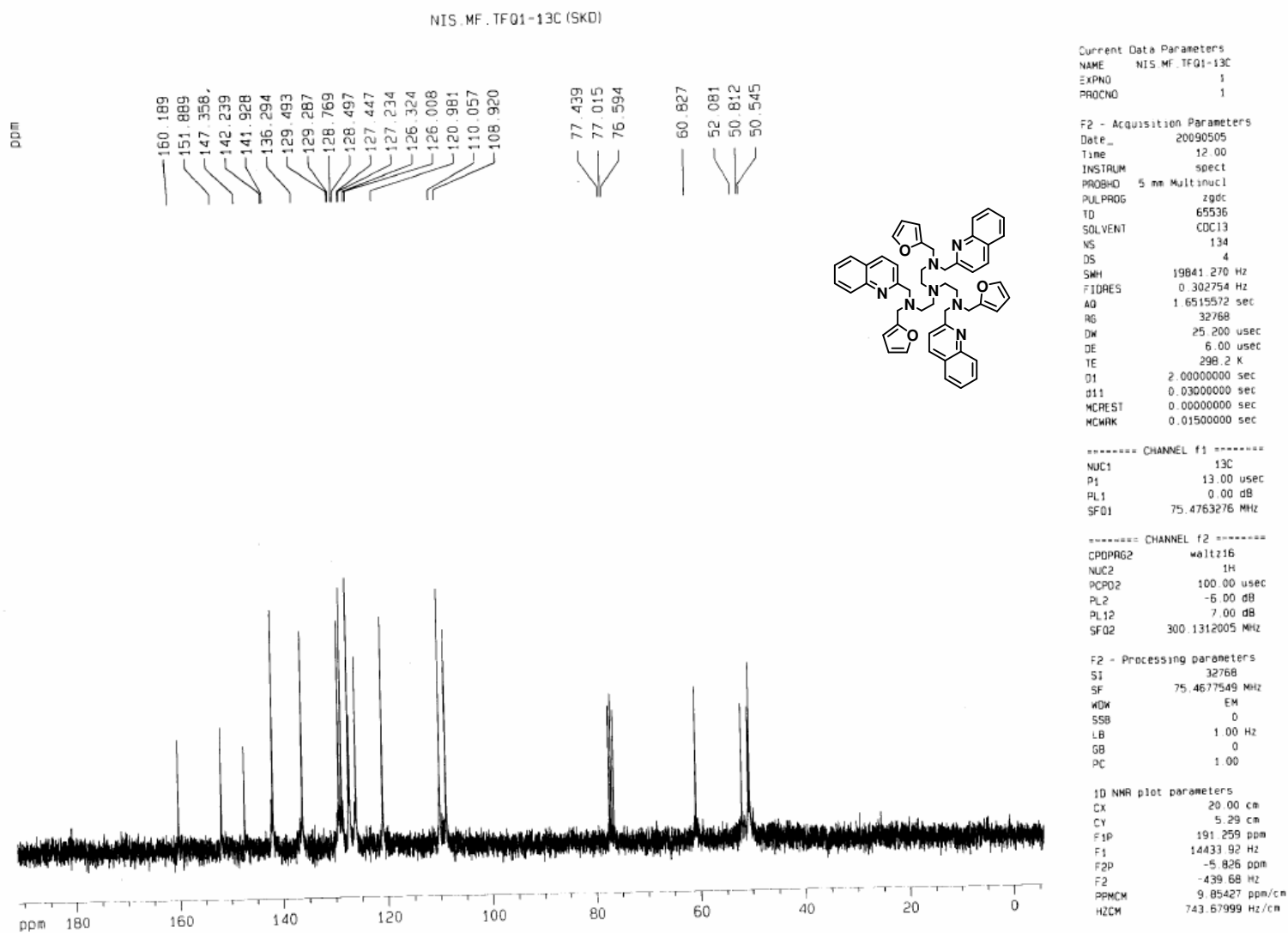


Figure S5. ^{13}C NMR Spectrum of **2** in CDCl_3

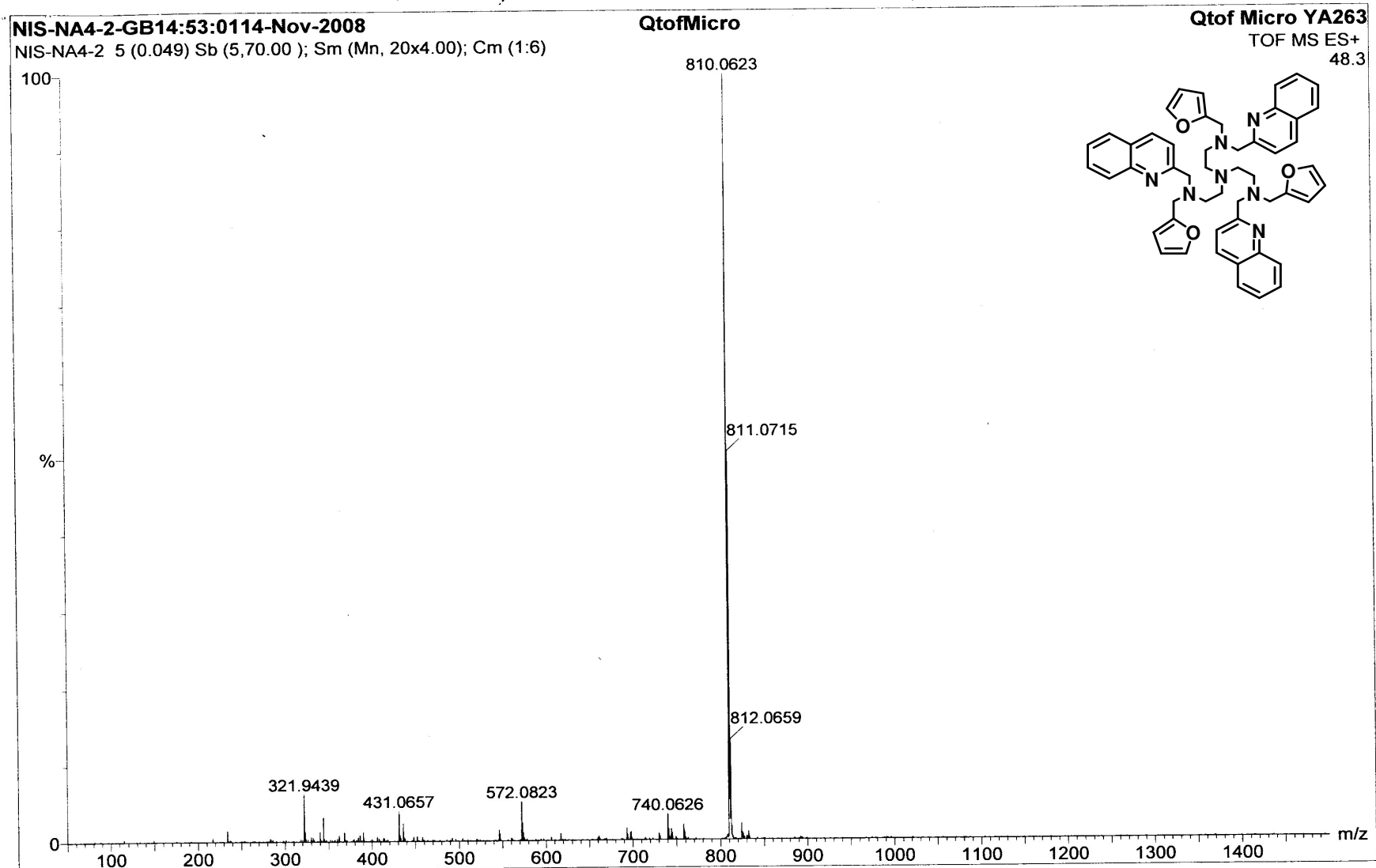


Figure S6. HRMS spectrum of **2**

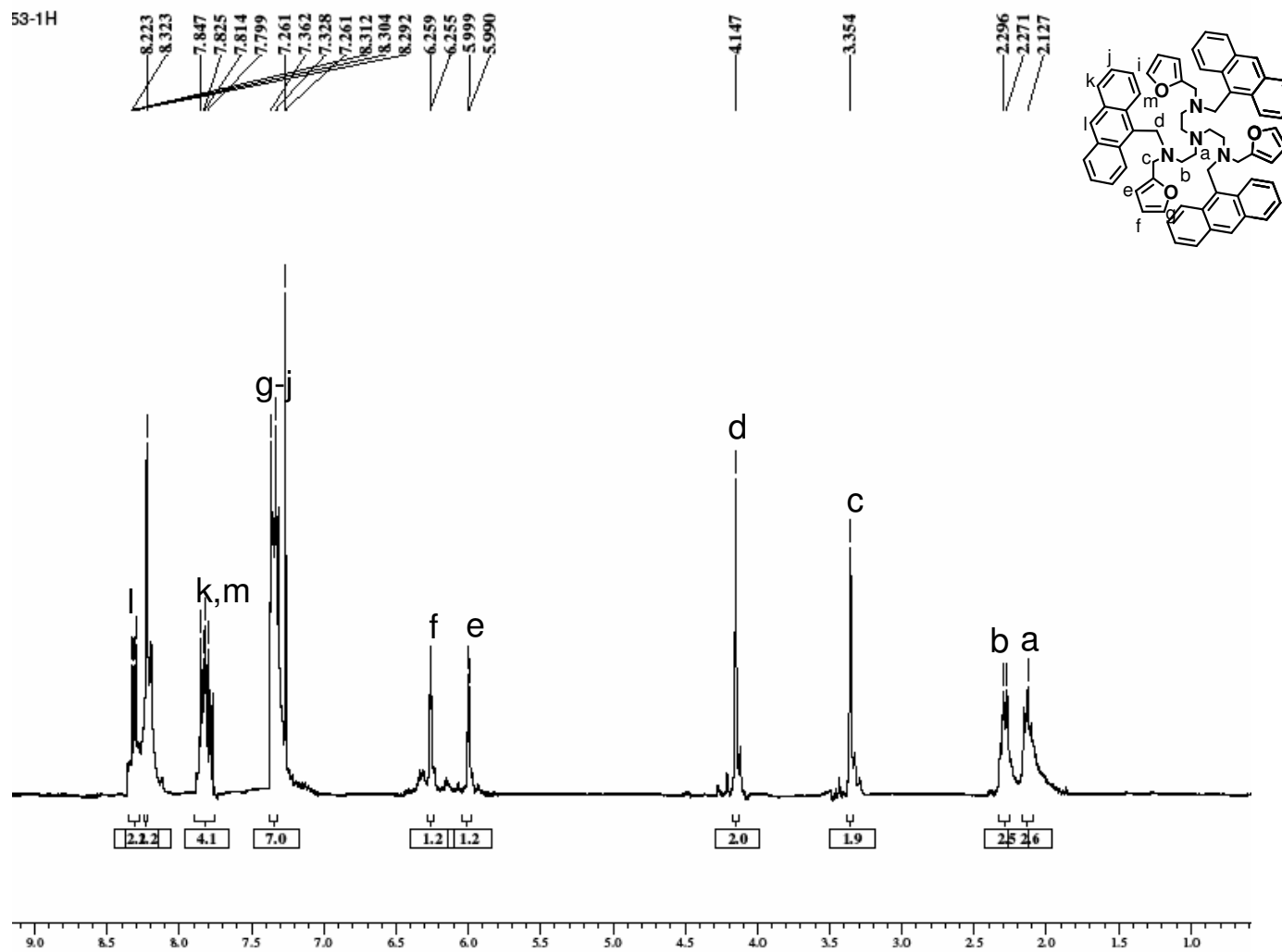


Figure S7. ^1H NMR Spectrum of 3 in CDCl_3

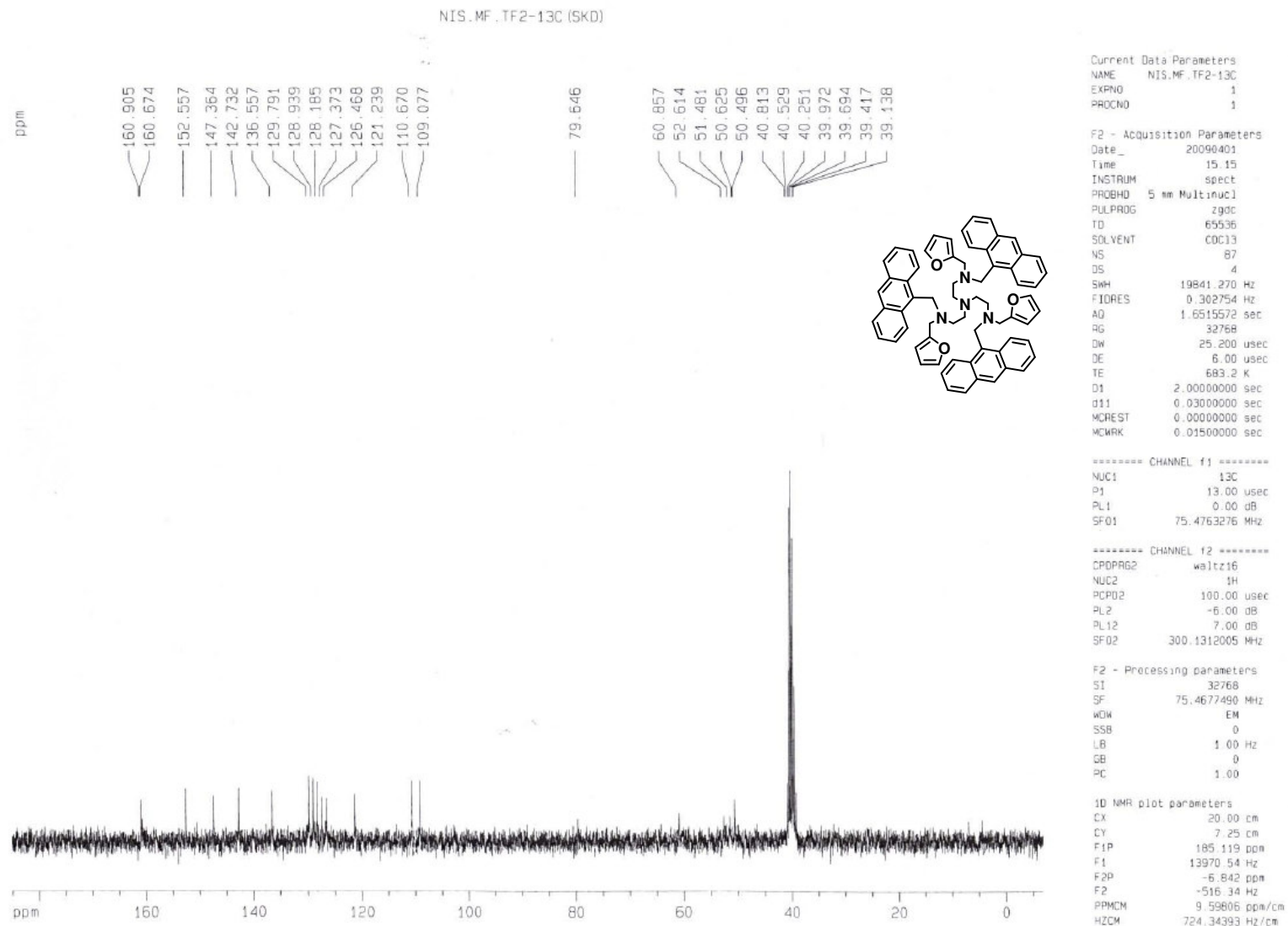


Figure S8. ^{13}C -NMR spectrum of 3 in DMSO-d₆

NISMF-53-GB11:20:4209-Apr-2009

QtofMicro

Qtof Micro YA263

NISMF-53 2 (0.020) Sb (5,70.00); Sm (Mn, 20x4.00); Cm (1:6)

TOF MS ES+

100- 191.0375

6.33

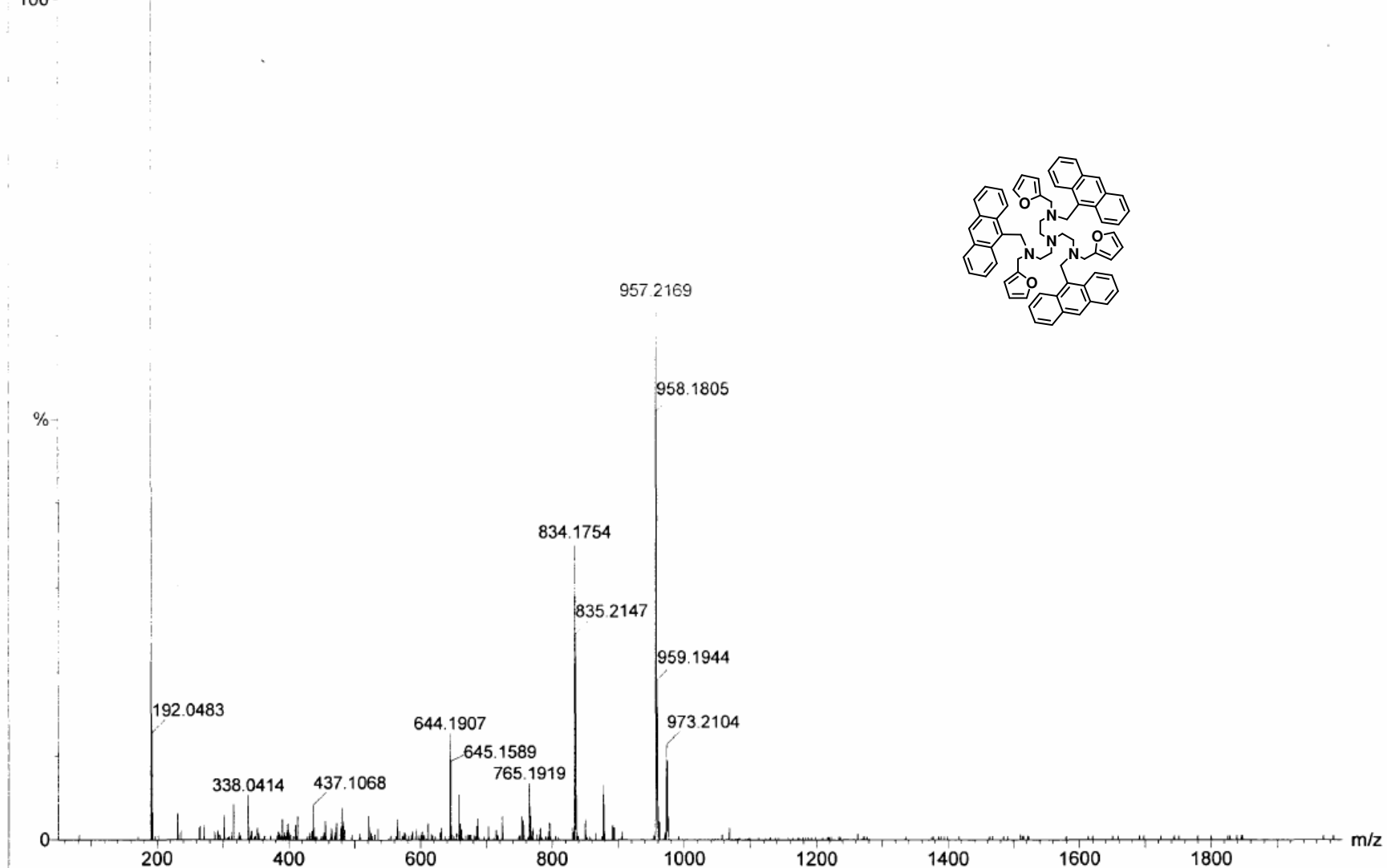


Figure S9. HRMS spectrum of 3

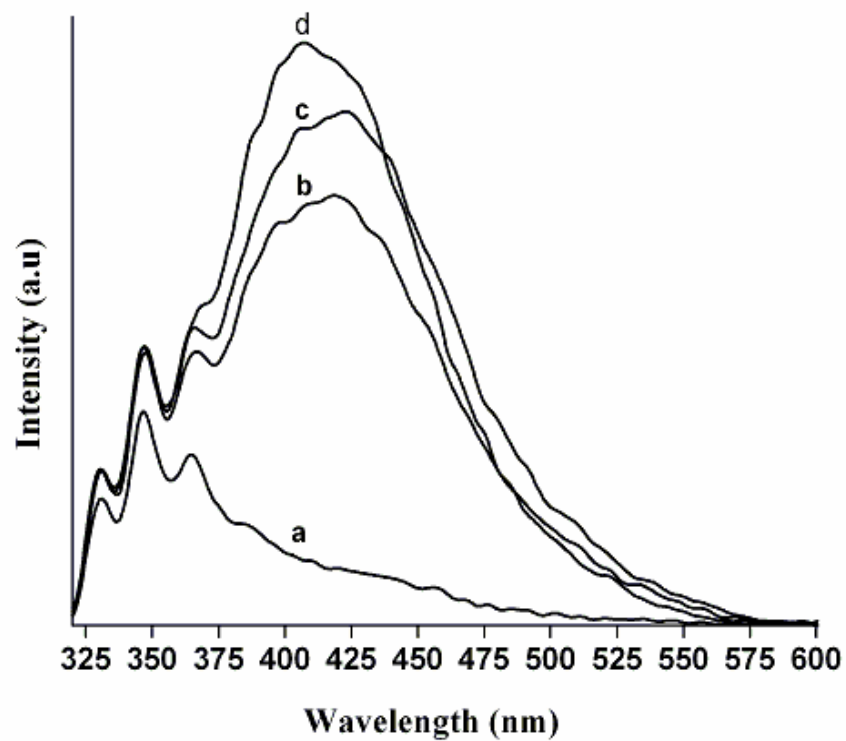


Figure S10. Variation of the Emission spectra of (a) **2** (5×10^{-6} M) in CH₃CN. (b) Upon addition of 100 equiv of Hg²⁺ to 'a'. (c) Upon addition of 100 equiv of Hg²⁺ and Cu²⁺ to 'a'. (d) Upon addition of 100 equiv of Hg²⁺ and Zn²⁺ to 'a'. $\lambda_{\text{exc}} = 315$ nm.

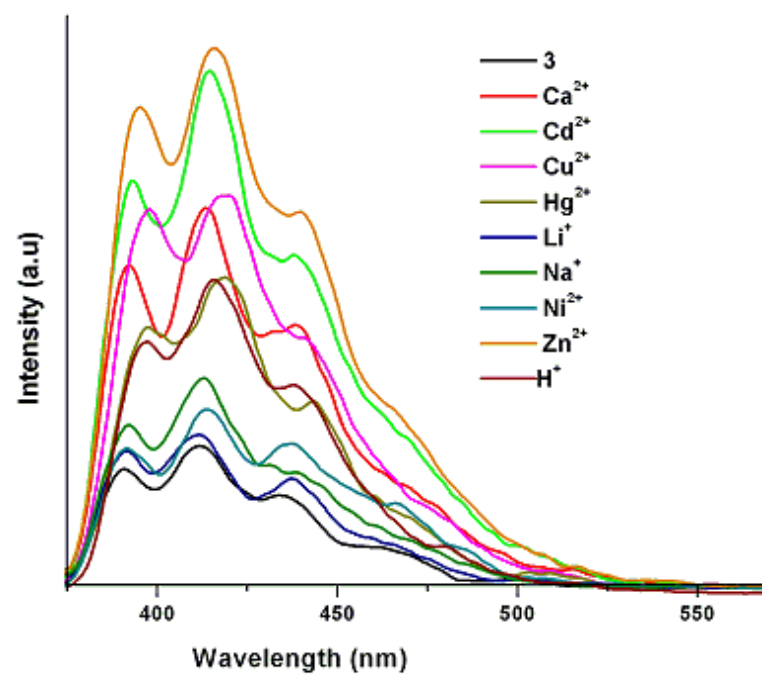


Figure S11. Fluorescence response of **3** (1×10^{-7} M) with different metal ions in THF at 298 K. $\lambda_{\text{exc}} = 368$ nm.

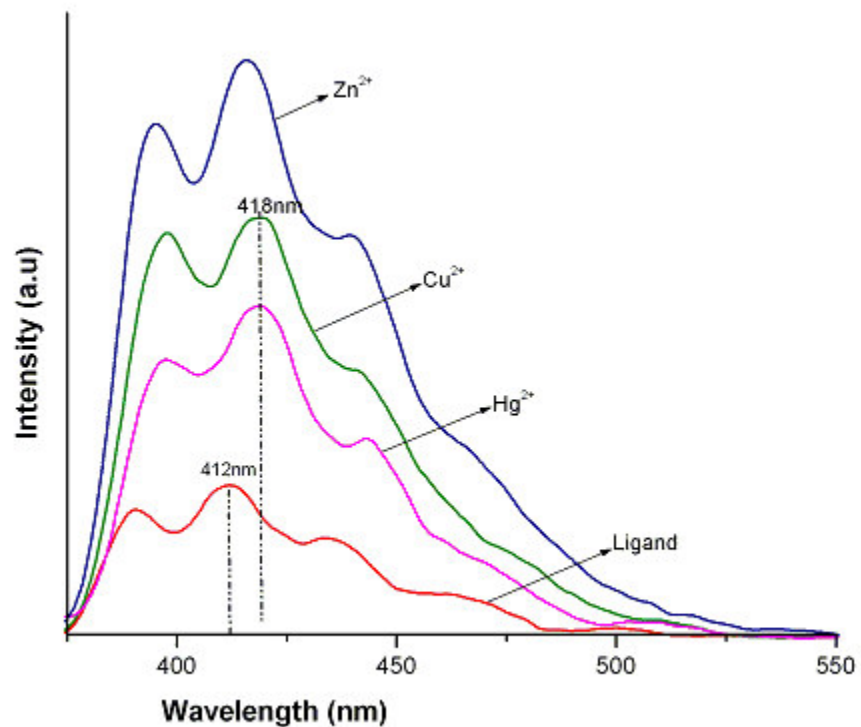


Figure S12. Fluorescence response of **3** (1×10^{-7} M) with 100 equiv of Cu^{2+} , Hg^{2+} and Zn^{2+} in THF at 298 K with maximum 6 nm spectral shift for the addition of Cu^{2+} . $\lambda_{\text{exc}} = 368$ nm.

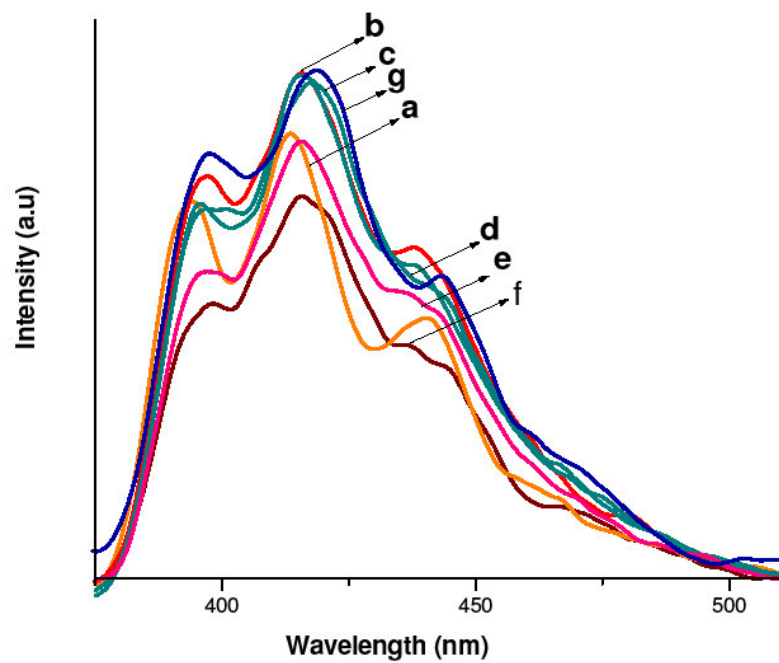


Figure S13. Emission spectra of (a) **3** (1×10^{-7} M) in THF; (b) **3** (1×10^{-7} M) in THF in presence of 0.02N HCl; (c) Solution 'b' containing of 4×10^{-6} M Hg^{2+} ; (d) 1×10^{-4} M Hg^{2+} ; (e) 1×10^{-3} M Hg^{2+} ; (f) 1.8×10^{-3} M Hg^{2+} . $\lambda_{\text{exc}} = 368$ nm

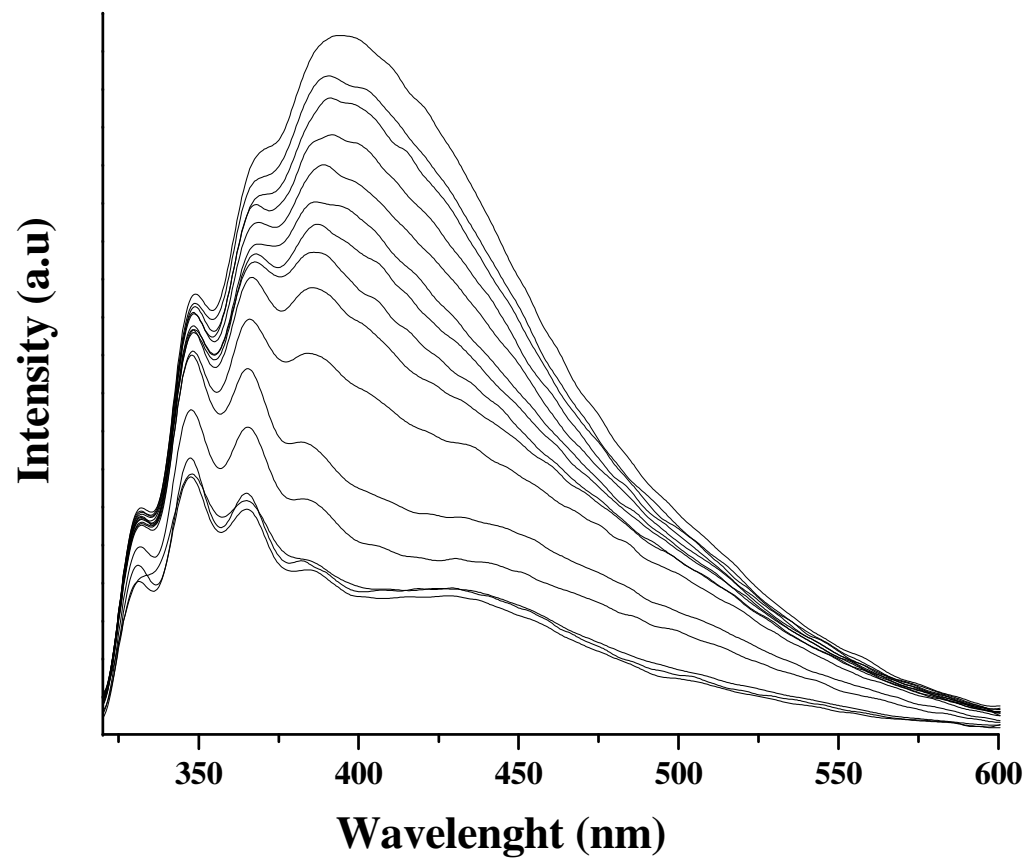


Figure S14. Fluorometric titration of **2** (5×10^{-6} M) with different concentrations of Zn^{2+} in CH_3CN . $\lambda_{\text{exc}} = 315$ nm.

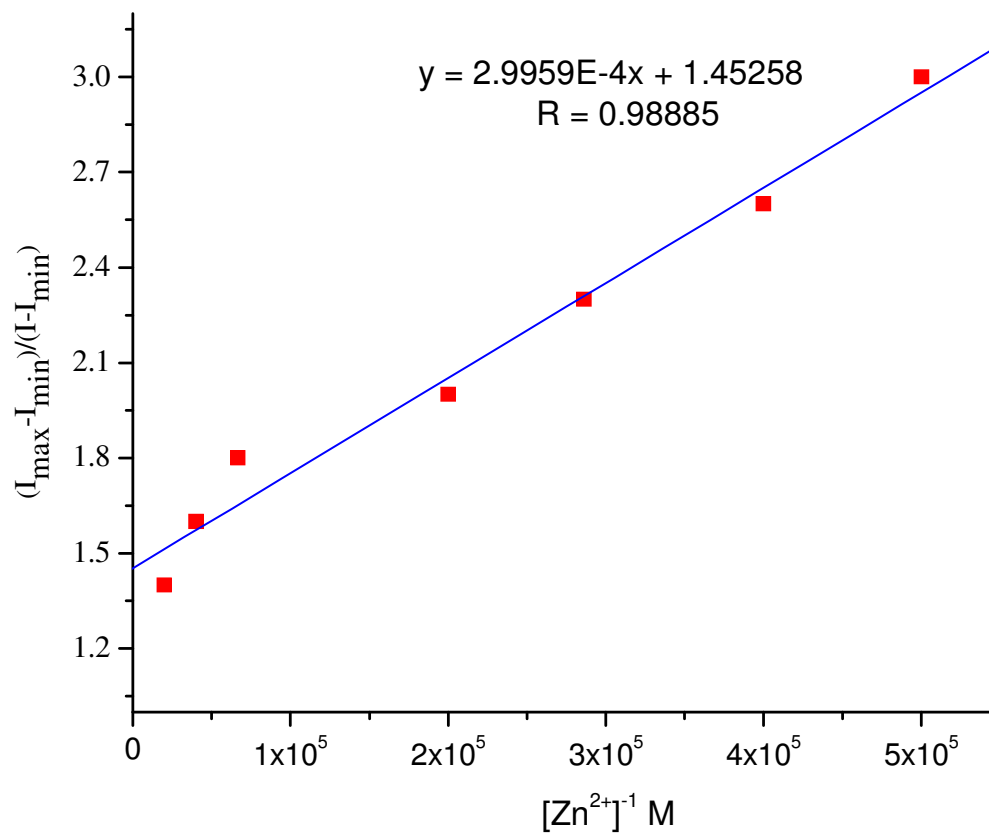


Figure S15. Benesi-Hiderband Linear Plot for **2** with different concentrations of Zn(II) at 298 K. $\lambda_{exc} = 315$ nm.

Plot of $(I_{\max} - I_{\min}) / (I - I_{\min})$ against $[Zn^{2+}]^{-1}$ for **2**.

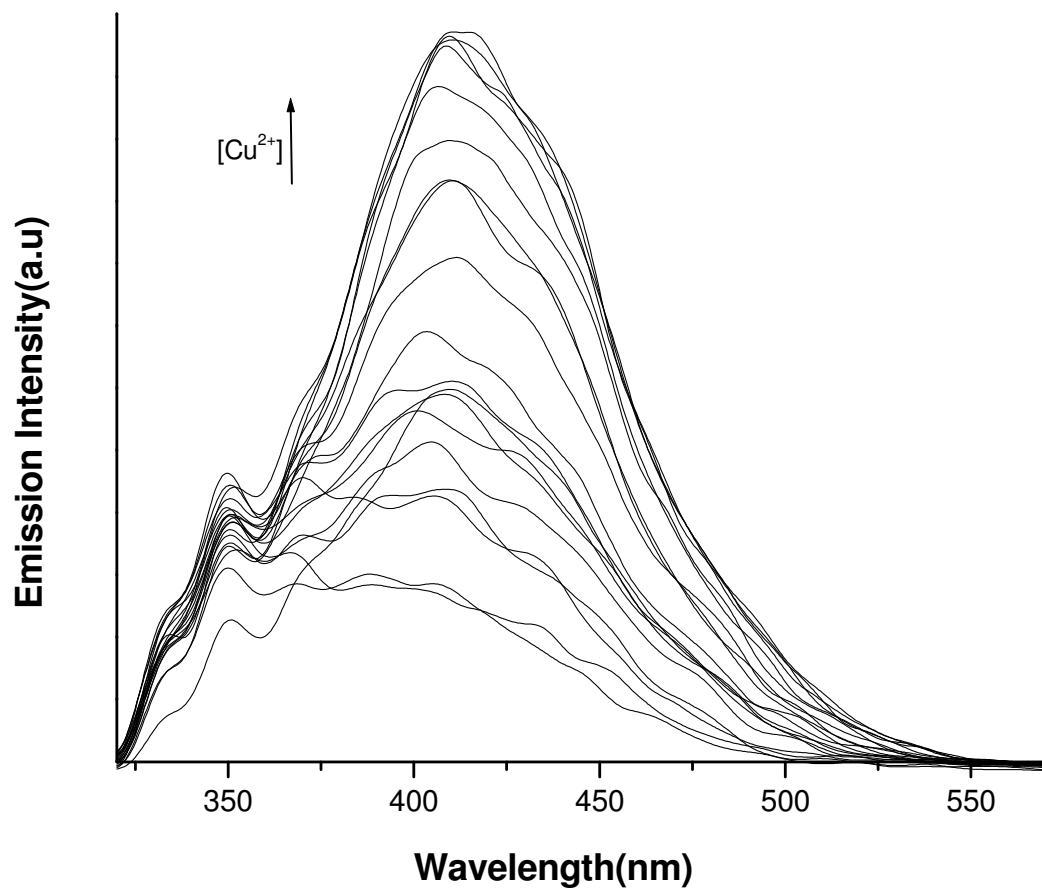


Figure S16. Fluorometric titration of **2** (5×10^{-6} M) with different concentrations of Cu^{2+} in CH_3CN . $\lambda_{\text{exc}} = 315$ nm

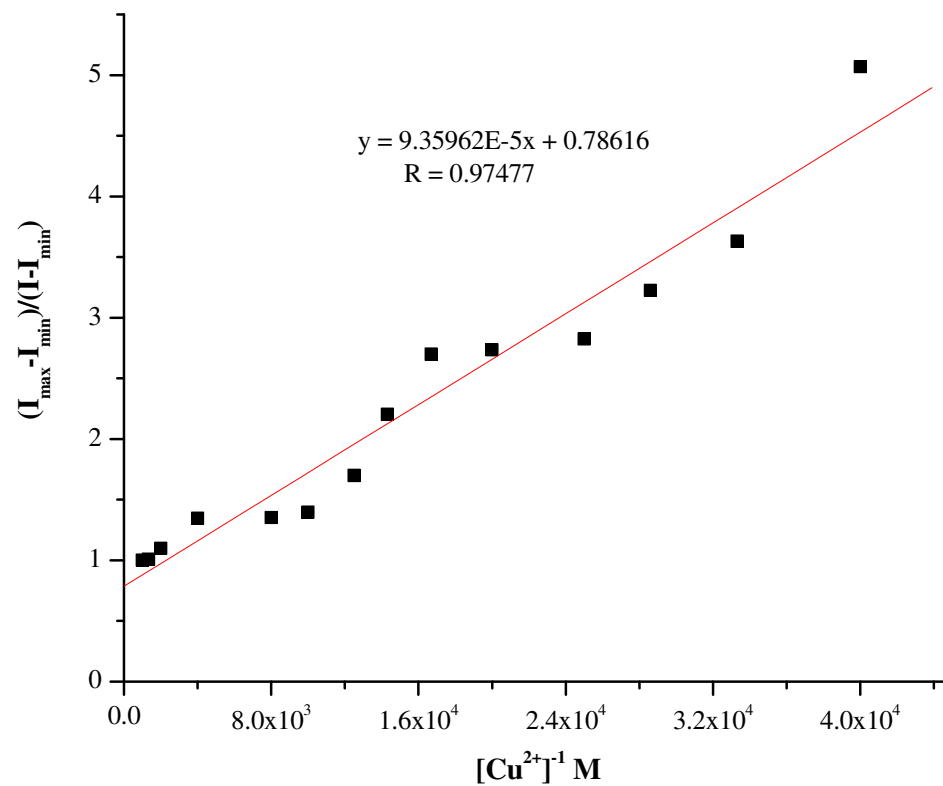


Figure S17. Benesi-Hiderband Linear Plot for **2** with different concentrations of Cu(II) at 298 K. $\lambda_{\text{exc}} = 315 \text{ nm}$.

Plot of $(I_{\max} - I_{\min}) / (I - I_{\min})$ against $[Cu^{2+}]^{-1}$ for **2**

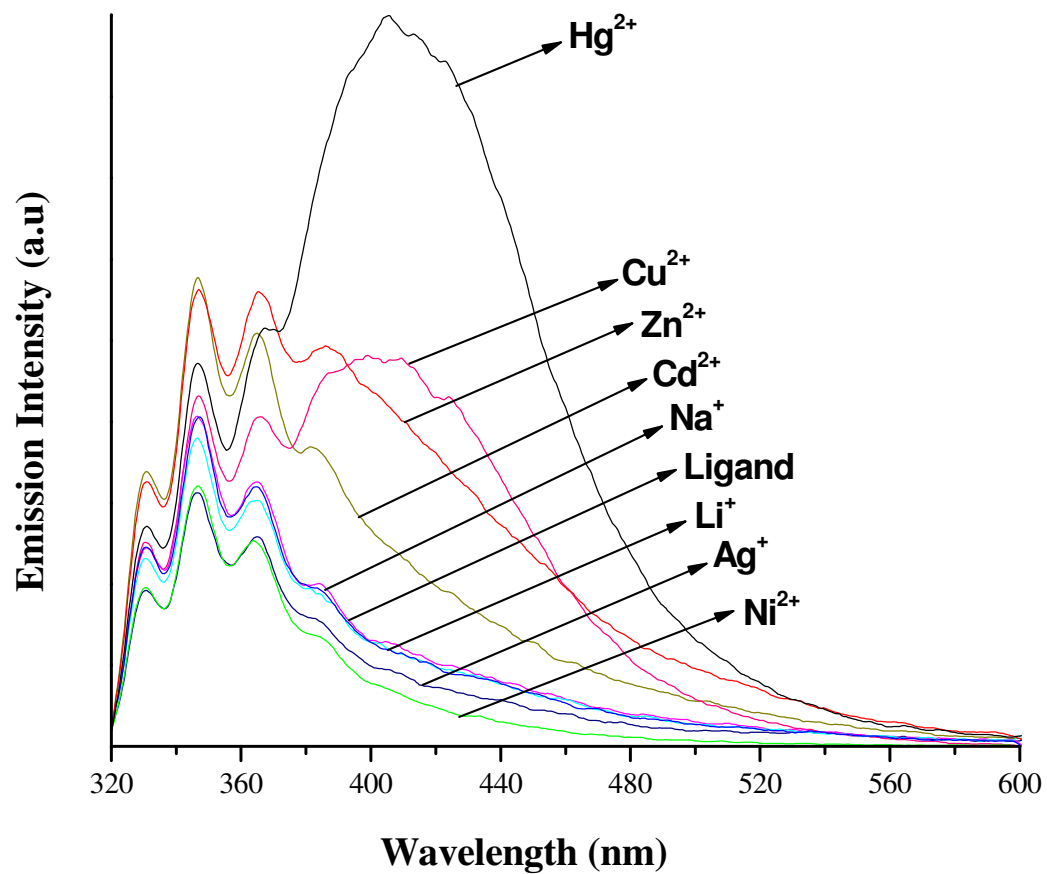


Figure S18. Fluorescence response of **2** (5×10^{-6} M) with 100 equiv. of different metal ions in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (8:2, v/v) at 298 K. $\lambda_{\text{exc}} = 315$ nm

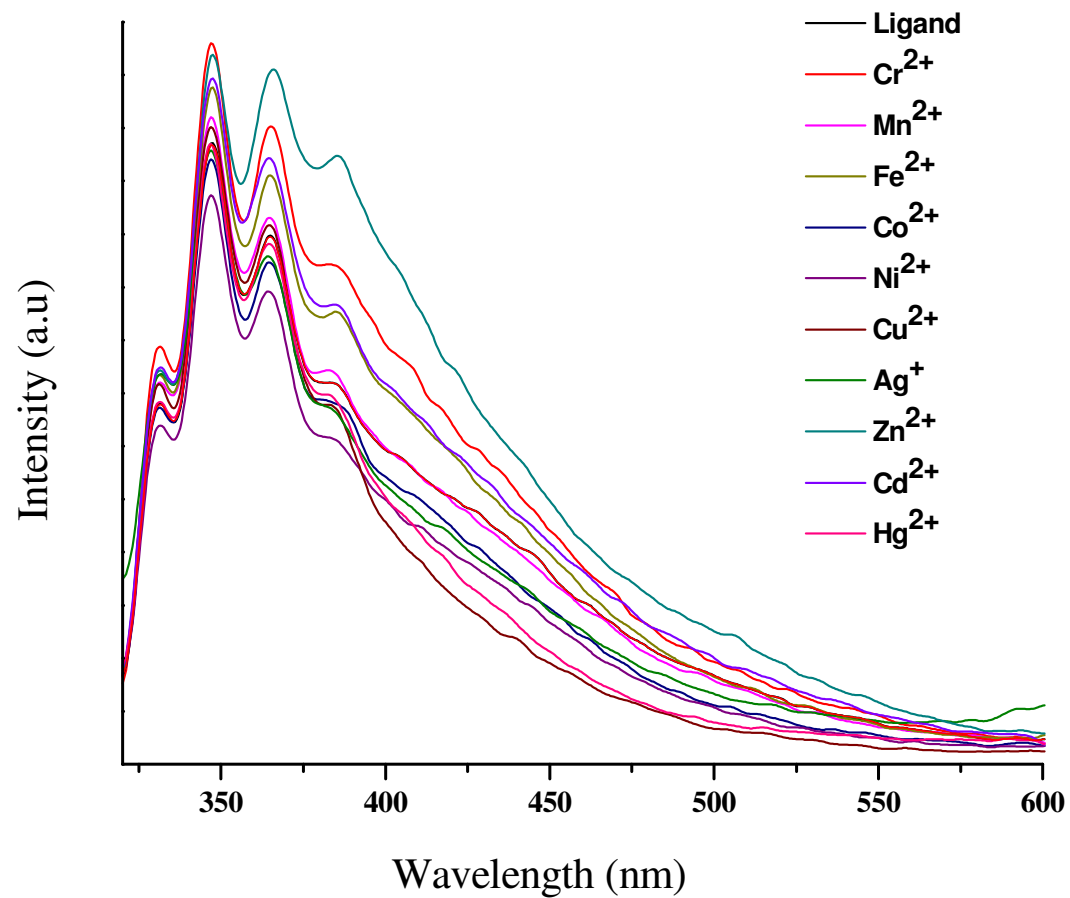


Figure S19. Fluorescence response of 2 (5×10^{-6} M) with 100 equiv. of different metal ions in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (1:1, v/v)

at 298 K. $\lambda_{\text{exc}} = 315$ nm

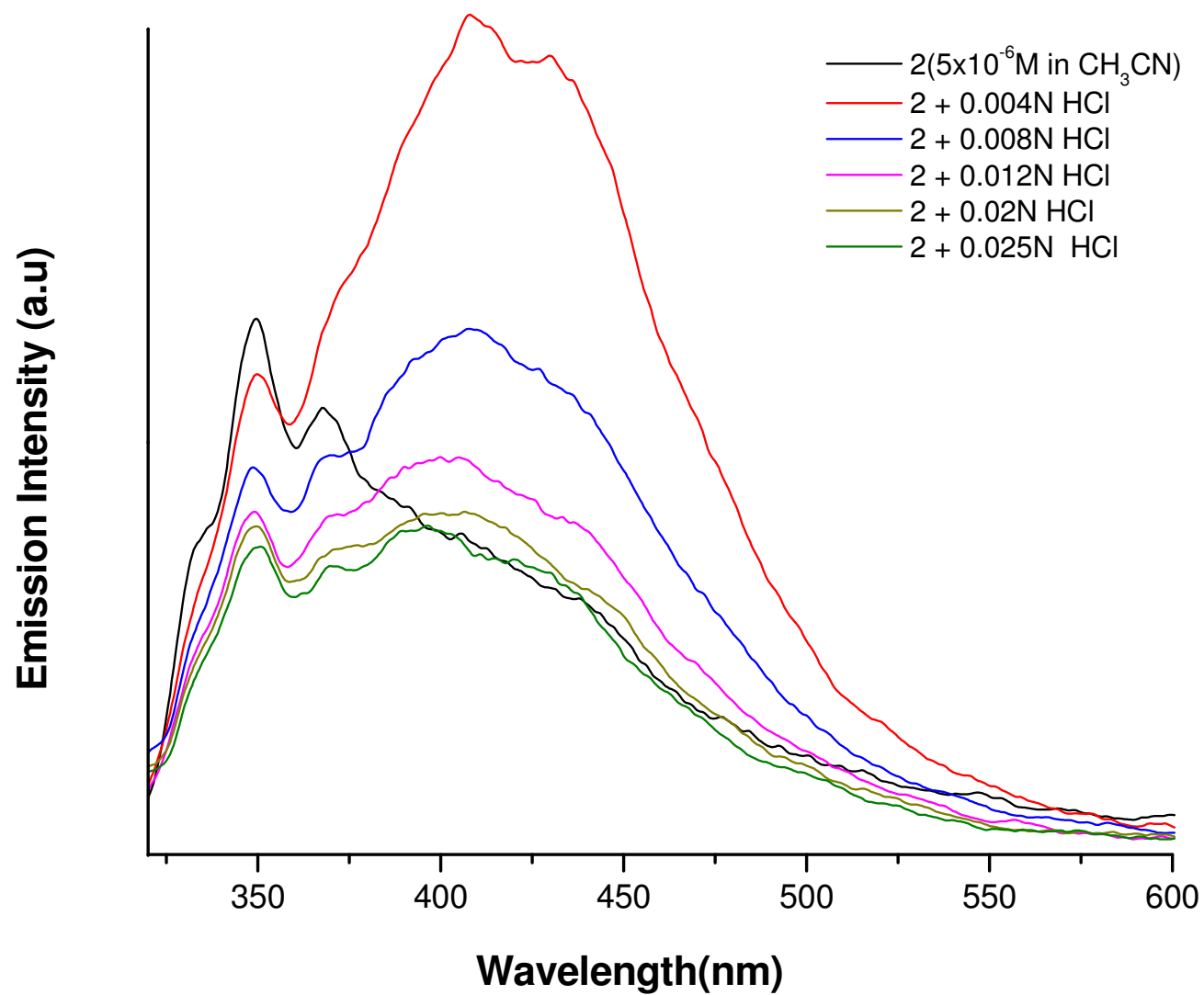


Figure S20. Emission spectra of **2** (5×10^{-6} M) in CH_3CN in presence of various H^+ concentration.

Methods.

The binding constant value of Hg^{2+} with **2** has been determined from the emission intensity data following the modified Benesi–Hildebrand equation.²

$$1/\Delta I = 1/\Delta I_{\max} + (1/K[\text{Hg}^{2+}])(1/\Delta I_{\max}).$$

Here, $\Delta I = I - I_{\min}$, $\Delta I_{\max} = I_{\max} - I_{\min}$.

Where, I_{\min} , I , I_{\max} are the intensities of **2** considered in the absence of Hg^{2+} , at an intermediate and at a concentration of complete concentration.

K is binding constant, $[\text{Hg}^{2+}]$ is concentration of Hg^{2+} .

From the Plot of $(I_{\max} - I_{\min}) / (I - I_{\min})$ against $[\text{Hg}^{2+}]^{-1}$ for **2**, the value of K ($\pm 10\%$) extracted from the slope is $1.7 \times 10^4 \text{M}^{-1}$.

References.

1. Lan, P.; Berta, D.; Porco, J. A.; South, M. S.; J. Parlow, J. J. *J. Org. Chem.*, **2003**, *68*, 9678-9686.
2. (a) Mallick, A.; Chattopadhyay, N. *Photochem. Photobiol.* **2005**, *81*, 419–424. (b) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707.