Supporting Information

Triphenylene based copper ensemble for the detection of cyanide ions.

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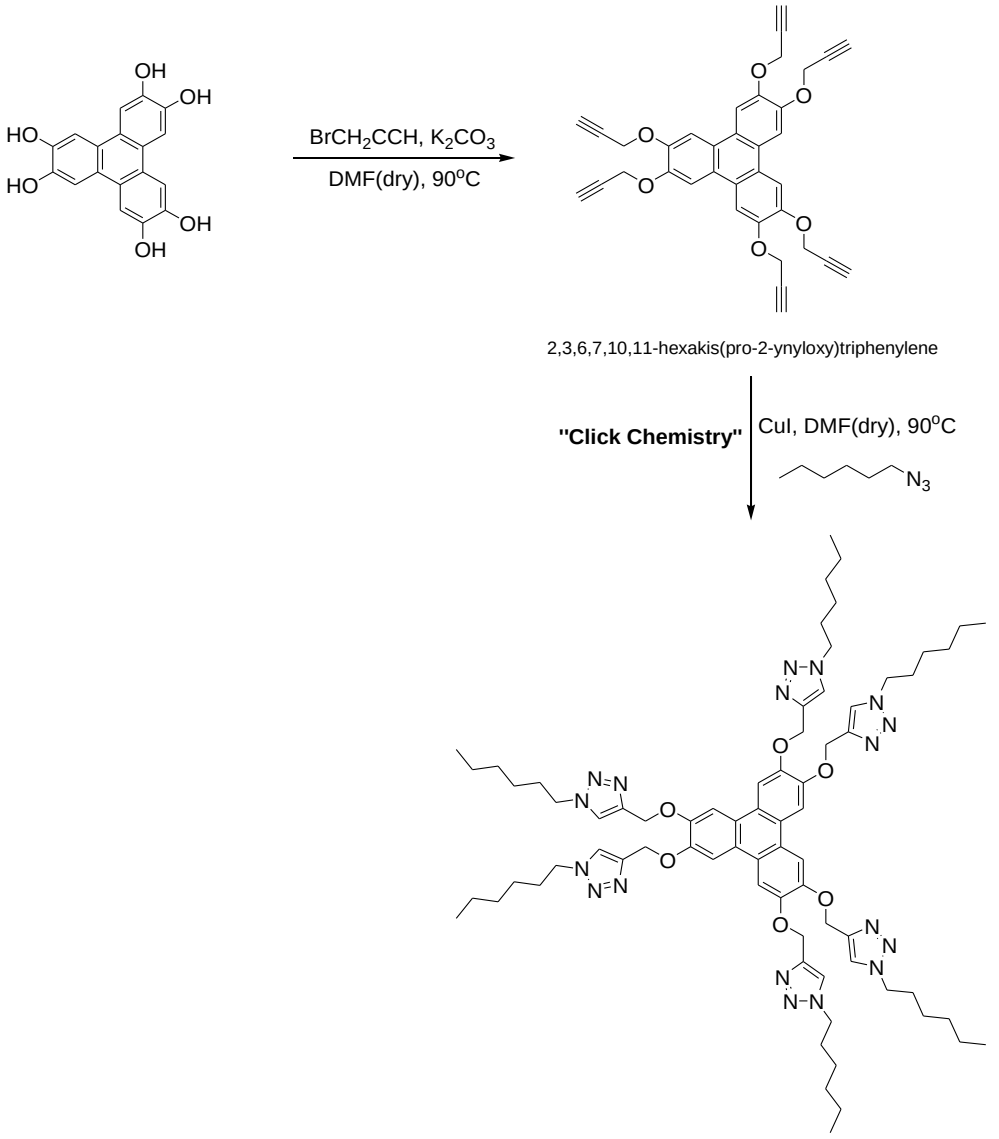
General information

All reagents were purchased from Aldrich and were used without further purification. THF was dried over sodium and benzophenone and kept over molecular sieves overnight before use. UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length 1 cm). The cell holder was thermostatted at 25°C. The fluorescence spectra were recorded with a SHIMADZU 5301 PC spectrofluorimeter. Elemental analysis was done using a Flash EA 1112 CHNS/O analyzer from Thermo Electron Corporation. ^{1}H and ^{13}C spectra were recorded on a JEOL-FT NMR-AL 300 MHz spectrophotometer using $CDCl_3$ as solvent and tetramethylsilane as the internal standard. Data are reported as follows: chemical shift in ppm (d), multiplicity (s = singlet, d = doublet, t = triplet,m = multiplet, br = broad singlet), coupling constants J (Hz), integration and interpretation.

Synthetic scheme for compound 1

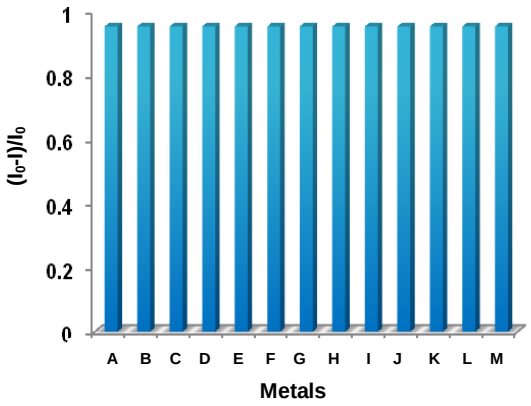


4-((2,3,6,7,10-pentakis((1-hexyl-1H-1,2,3-triazol-4-yl)methoxy)triphenylen-11-yloxy)methyl)-1-hexyl-1H-1,2,3-triazole (1; 58%)

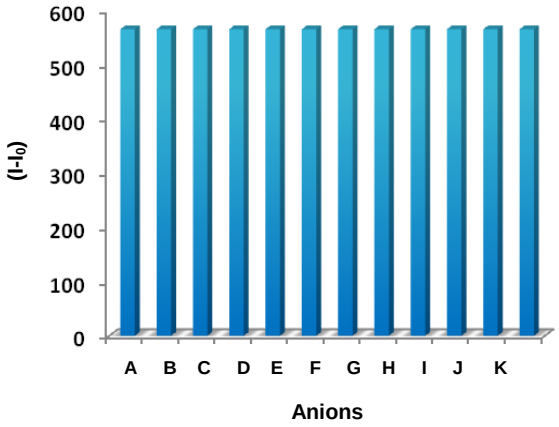
Scheme 1

Synthesis of 2,3,6,7,10,11-hexakis(*pro-2-ynyloxy*)triphenylene: To a solution of hexahydroxytriphenylene (900 mg, 2.77 mmol) in dry DMF (5 ml) was added K_2CO_3 (3.45 g, 25 mmol), and mixture was stirred at room temperature for 10-15 minutes. Then propargyl bromide (2.97 g, 25 mmol) was added drop-wise and slowly with continues stirring the reaction mixture. The resulting mixture was heated at 60-70°C overnight. After the completion of reaction, added excess of water. The solid was separated out, which was filtered off and washed with water to get the crude product. The crude was re-crystallized from DCM and methanol to get the titled compound as yellow solid in 70% yield. ^{1}H NMR (300 MHz, DMSO-d_6, δ ppm): 3.62 (s, 6 H), 5.09 (s, 12 H), 8.13 (s, 6 H); ^{13}C NMR (75.45 MHz, DMSO-d_6, δ ppm): 56.51, 78.68, 79.06, 107.82, 123.21, 146.83; (FAB+) MS m/z: 576 $(M+Na)^+$. Elemental analysis: calcd. for $C_{36}H_{24}O_6$: C 78.25, H 4.38; found: C 77.98, H 4.18

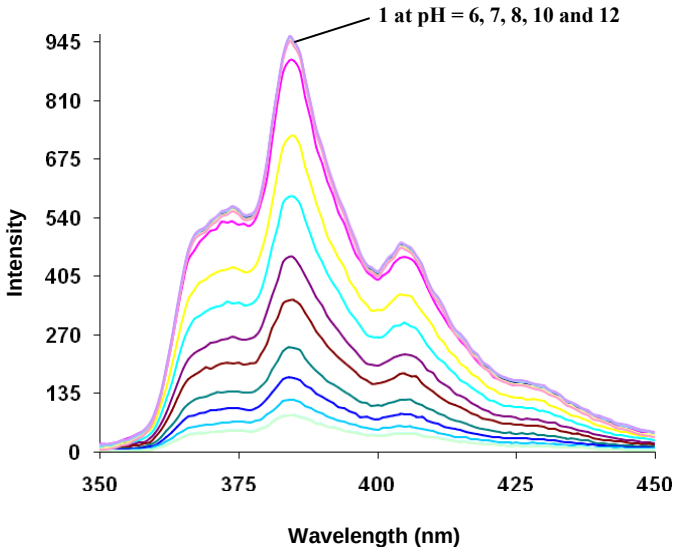
Synthesis of 4-((2,3,6,7,10-pentakis((1-hexyl-1H-1,2,3-triazol-4-yl)methoxy)triphenylen-11-yloxy)methyl)-1-hexyl-1H-1,2,3-triazole (1): A solution of 2,3,6,7,10,11-hexakis(*pro-2-ynyloxy*)triphenylene (706 mg, 1.27 mmol), hexylazide (1.17 g, 9.2 mmol) and Cu(I)I was heated in dry DMF (5-6 ml) at 90°C overnight. The mixture was then diluted with DCM and washed with water and then brine. The organic layer was separated, dried over Na_2SO_4 and the solvent was evaporated under reduce pressure to get the crude. The crude was purified from column chromatography to give the pure compound **1** as yellowish-brown solid in 58% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.82 (t, J = 6.9 Hz, 18 H), 1.25 (br, 36 H), 1.87 (s, 12 H), 4.33 (t, J = 7.2 Hz, 12 H), 5.55 (s, 12 H), 7.88 (s, 6 H), 8.06 (s, 6 H); ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 13.85, 22.32, 26.12, 30.17, 31.07, 50.35, 63.23, 108.07, 123.50, 123.69, 143.88, 147.81; MALDI-TOF MS m/z: 1317 $(M+2)^+$; Elemental analysis: calcd. for $C_{72}H_{101}N_{18}O_6$: C 65.78, H 7.74, N 19.18; Found: C 65.53, H 7.43, N 18.88.



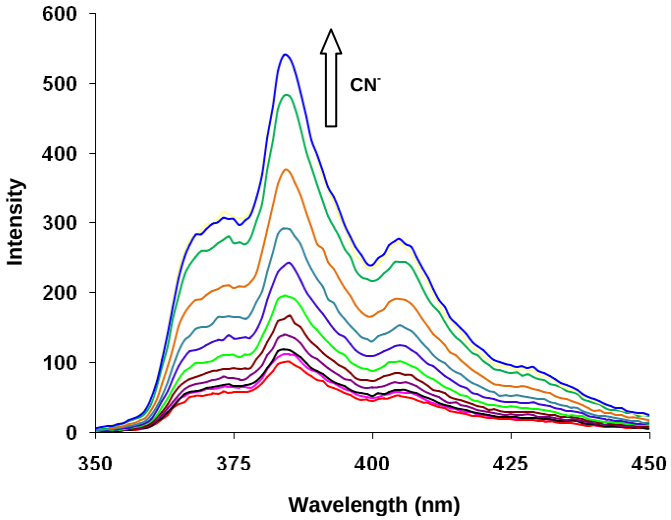
Competitive selectivity of **1** (2.5×10^{-6} M) towards different metals ions; A=Cu^{2+}, B=Zn^{2+}, C=Co^{2+}, D=Pb^{2+}, E=Ni^{2+}, F=Cd^{2+}, G=Ag^{+}, H=Ba^{2+}, I=Ca^{2+}, J=Mg^{2+}, K=K^{+}, L=Na^{+}, M=Li^{+} in DMSO.



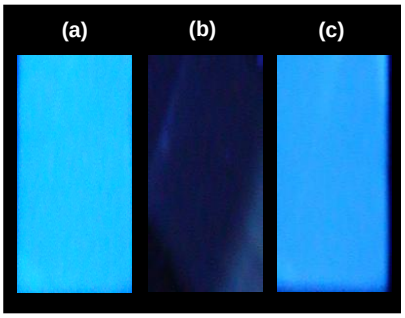
Competitive selectivity of ensemble **1-Cu**$^{2+}$ towards the CN^- over the other anions. (A=CN^-, B=F^-, C=Cl^-, D=Br^-, E=I^-, F=CH_3COO^-, G= NO_3^-, H= $H_2PO_4^-$, I= ClO_4^-, J=OH^-, K=CO_3^{2-}, L=SO_4^{2-}) in DMSO.



Fluorescence spectra of **1** (2.5×10^{-6} M) in response to addition of Cu^{2+} ions (250 equiv.) in DMSO:H_2O (90:10) in the pH range of 6-12.



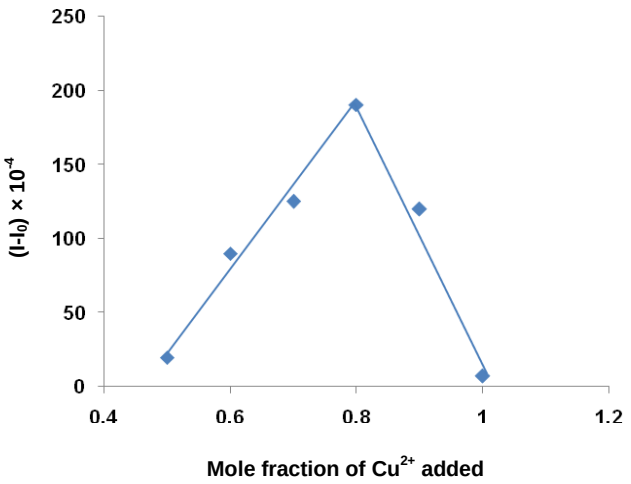
Fluorescence spectra of **1.Cu**$^{2+}$ ensemble upon the addition of incremental amount of NaCN (250 equiv.) in tap H_2O.



Fluorescence images of TLC plates after running them in different solutions containing (a) DMSO solution of only 1 (b) DMSO solution containing 1+Cu^{2+} (c) water solution containing CN^- (excited at 365 nm using a UV lamp).

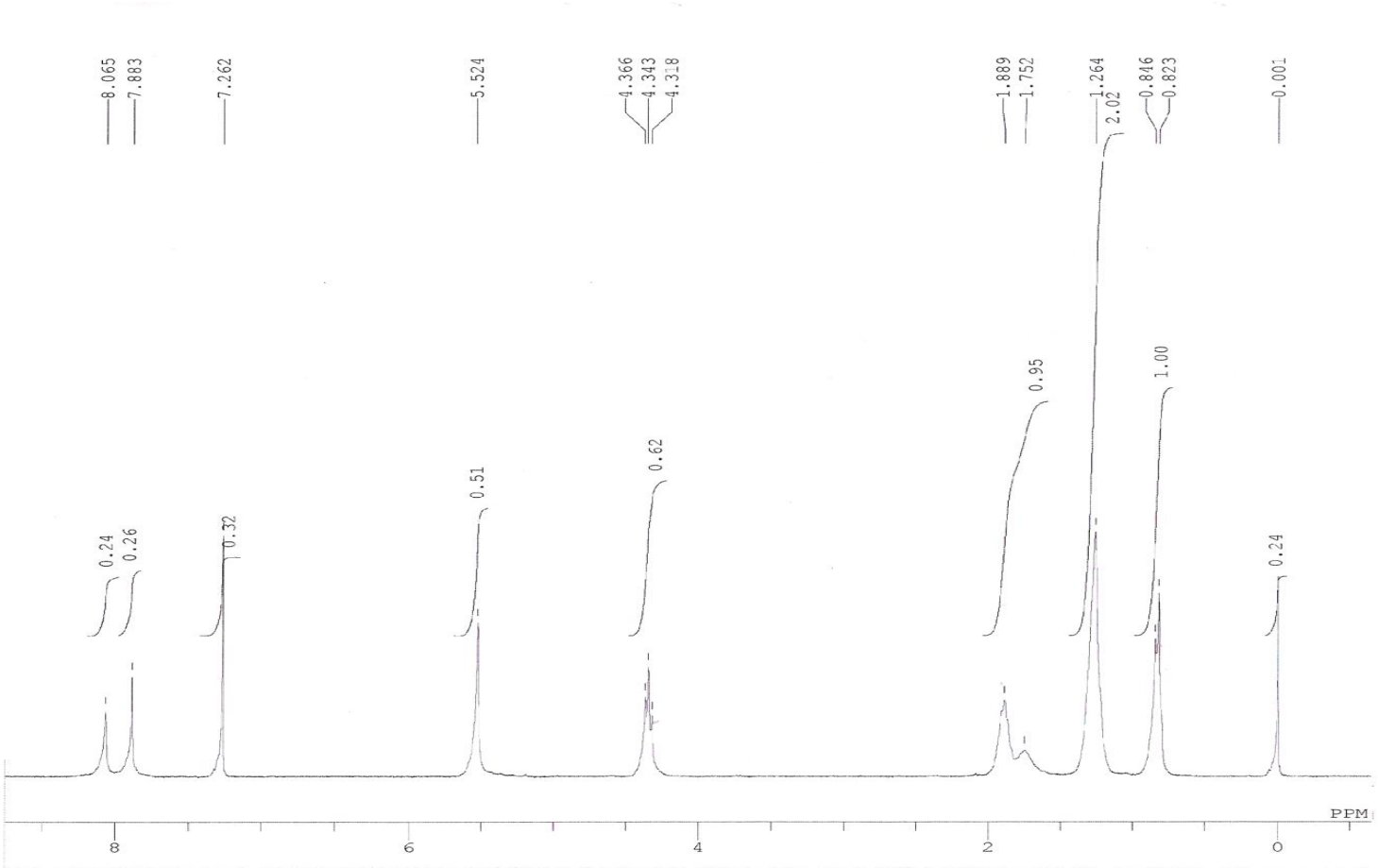
The significant improvement of **1-Cu^{2+}** system compared with that reported in references is given below.

S. No.	Publication	Practical applications of ensemble	Sensing ability of ensemble in tap water	Interference from other anions
1	Present Manuscript	Yes	Yes	No
2	*J. Mater. Chem.*, **2012**, 22, 1747-1750	No	No	No
3	*Org. Lett.*, **2011**, *13*, 5056–5059	No	No	No
4	*Org. Biomol. Chem.*, **2012**, 10, 555-560	No	No	Yes
5	*Tetrahedron*, **2010**, *66*, 7479-7486.	No	No	Yes
6	*Chem Comm*. 2010, *46*, 8953	No	No	No

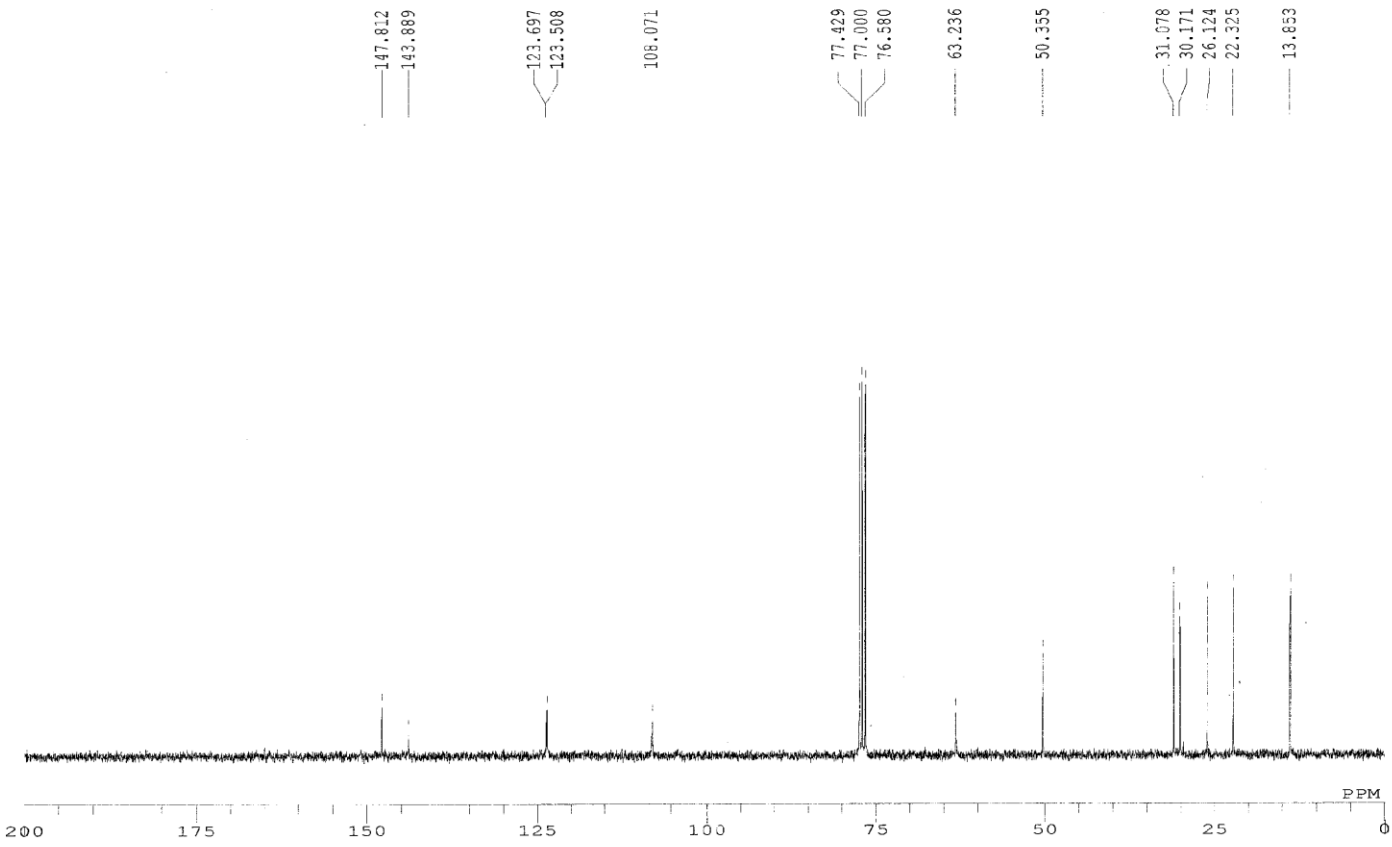


Job's plot to determining the stoichiometry of receptor **1** and Cu^{2+} ion in DMSO.

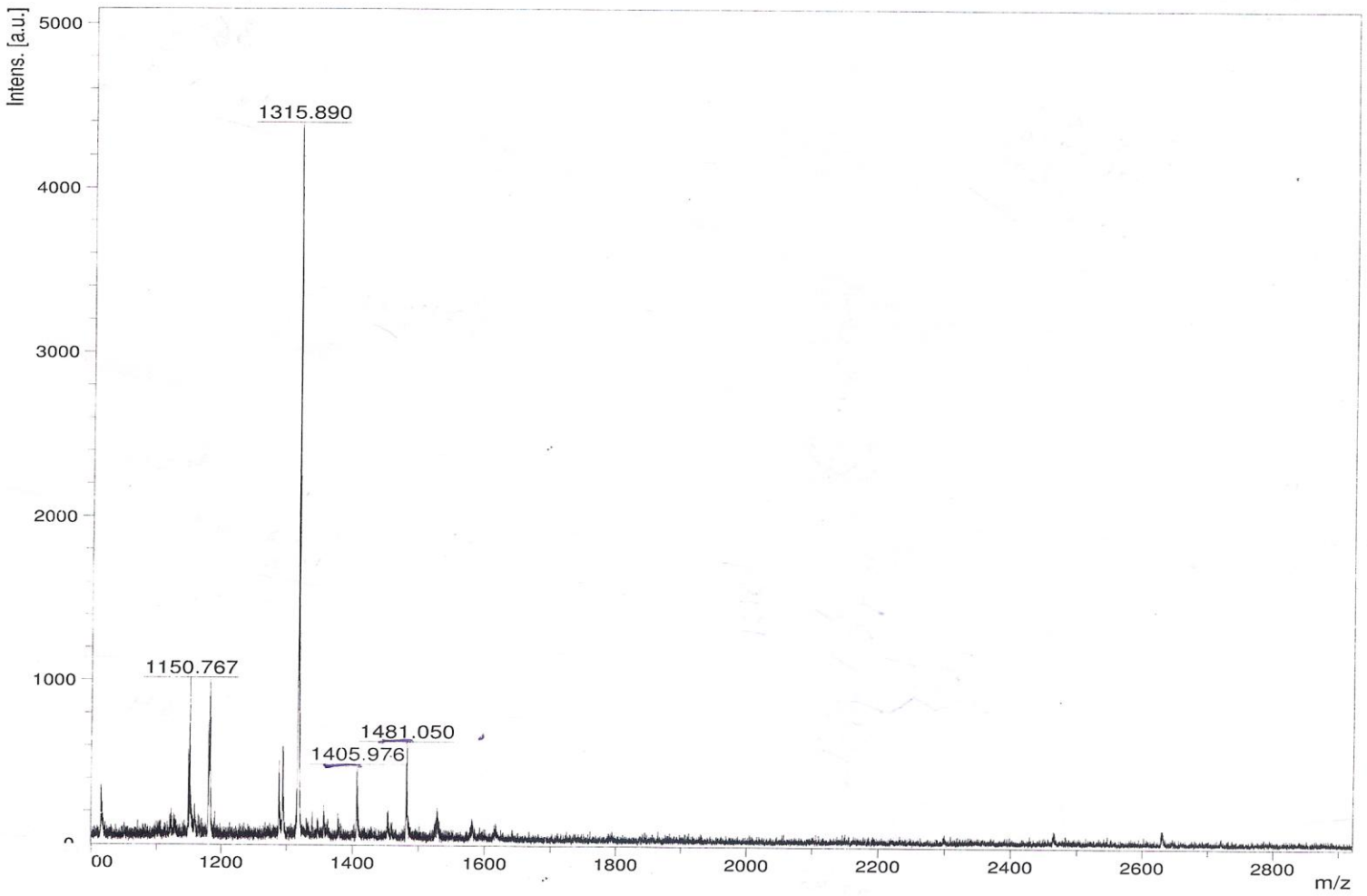
^{1}H NMR spectrum of Compound 1



^{13}C NMR spectrum of Compound 1



Mass spectrum of Compound 1



Mass spectrum of 1.Cu^{2+} complex