Electronic Supplementary Information

A new thiacalix[4]arene-fluorescein based probe for detection of CN^- and Cu^{2+} ions and construction of a sequential logic circuit

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S15 UV-vis spectra of adduct **3a** in presence of different metal ions in $CH_3CN:H_2O$ (8:2, v/v) buffered with HEPES, pH = 7.0.

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S24 UV-vis spectra of **3+CN$^-$+Cu^{2+}** in presence of CN^- ions in $CH_3CN:H_2O$ (8:2, v/v) buffered with HEPES, pH = 7.0.

S25 Fluorescence spectra of **3+CN$^-$+Cu^{2+}** in the presence of CN^- ions in $CH_3CN:H_2O$ (8:2, v/v) buffered with HEPES, pH = 7.0.

S26 Reversibility changes in absorbance spectra of receptor **3** on sequential addition of CN^- and Cu^{2+} in $CH_3CN:H_2O$ (8:2, v/v) buffered with HEPES, pH = 7.0.

S27 ^1H NMR spectrum of compound **2**

S28 Mass spectrum of compound **2**

General Experimental Procedure and quantum yield calculation:

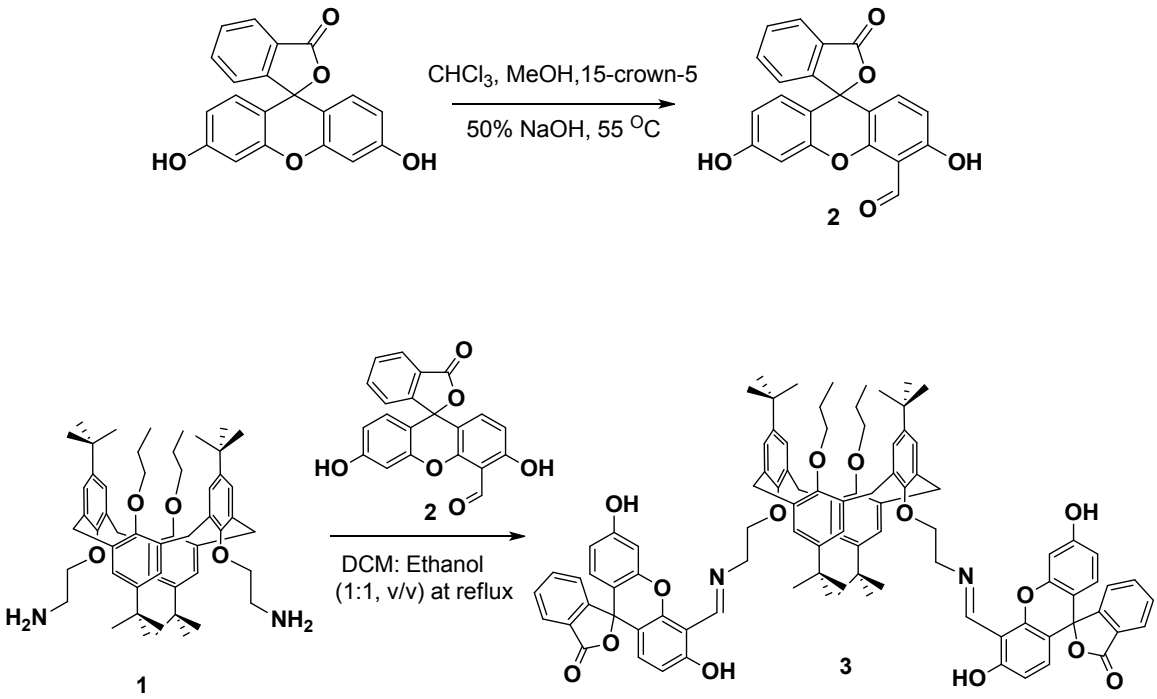
All reagents were purchased from Aldrich and were used without further purification. Acetonitrile (AR grade) was used to perform analytical studies. UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length, 1 cm). The cell holder was thermostatted at 25 °C. The fluorescence spectra were recorded with a SHIMADZU 5301 PC spectrofluorimeter. ^{1}H was recorded on a Bruker-AVANCE-II FT NMR-AL 500 MHz spectrophotometer using $CDCl_3$, DMSO-d_6 as solvent and tetramethylsilane $SiMe_4$ as internal standards. Mass spectra were recorded on a Bruker MicroTof QII mass spectrometer and MALDI-TOF. UV-vis studies were performed in CH_3CN and HEPES buffer (pH = 7.0). Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, br = broad, d = doublet, t = triplet, m = multiplet), coupling constants *J* (Hz), integration, and interpretation. Silica gel 60 (60–120 mesh) was used for column chromatography. Fluorescence quantum yield[1] was determined by using optically matching solution of fluorescence (Φ_{fr} = fluorescein) as standard at an excitation wavelength of 490 nm and quantum yield is calculated using the equation:

$$\Phi_{fs} = \Phi_{fr} \times \frac{1\text{-}10^{-ArLr}}{1\text{-}10^{-AsLs}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r}$$

Φ_{fs} and Φ_{fr} are the radiative quantum yields of sample and the reference respectively, A_s and A_r are the absorbance of the sample and the reference respectively, D_s and D_r the respective areas of emission for sample and reference. L_s and L_r are the lengths of the absorption cells of sample and reference respectively. N_s and N_r are the refractive indices of the sample and reference solutions.

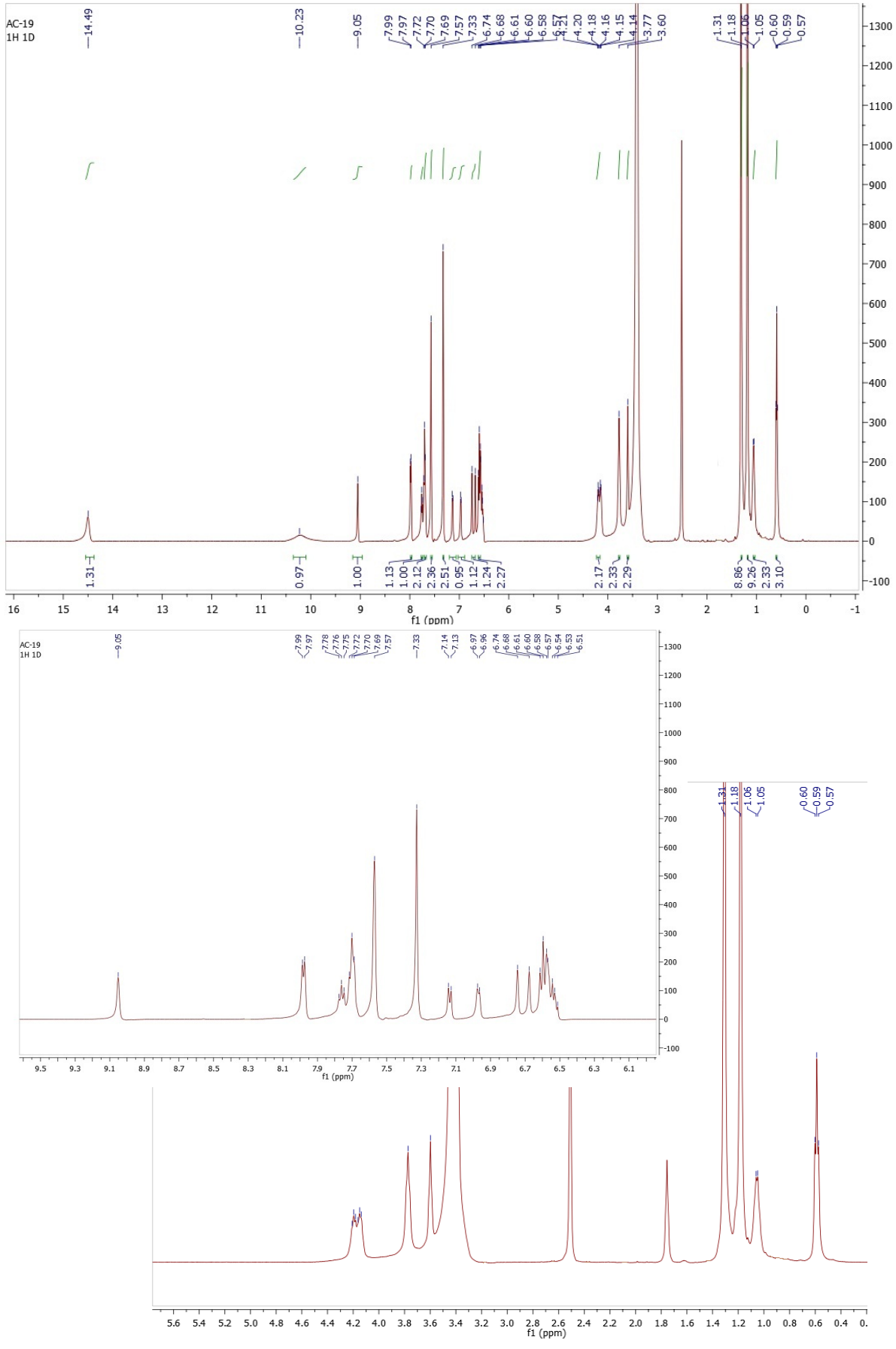
1 (*a*) Deams, J. N.; Grosby, G. A. *J. Phys. Chem.*, 1971, **75**, 991; (*b*) D. Magde, R. Wong and P. G. Seybold, *Photochem. Photobiol.,* 2002, **75**, 327–334.

Synthetic routes

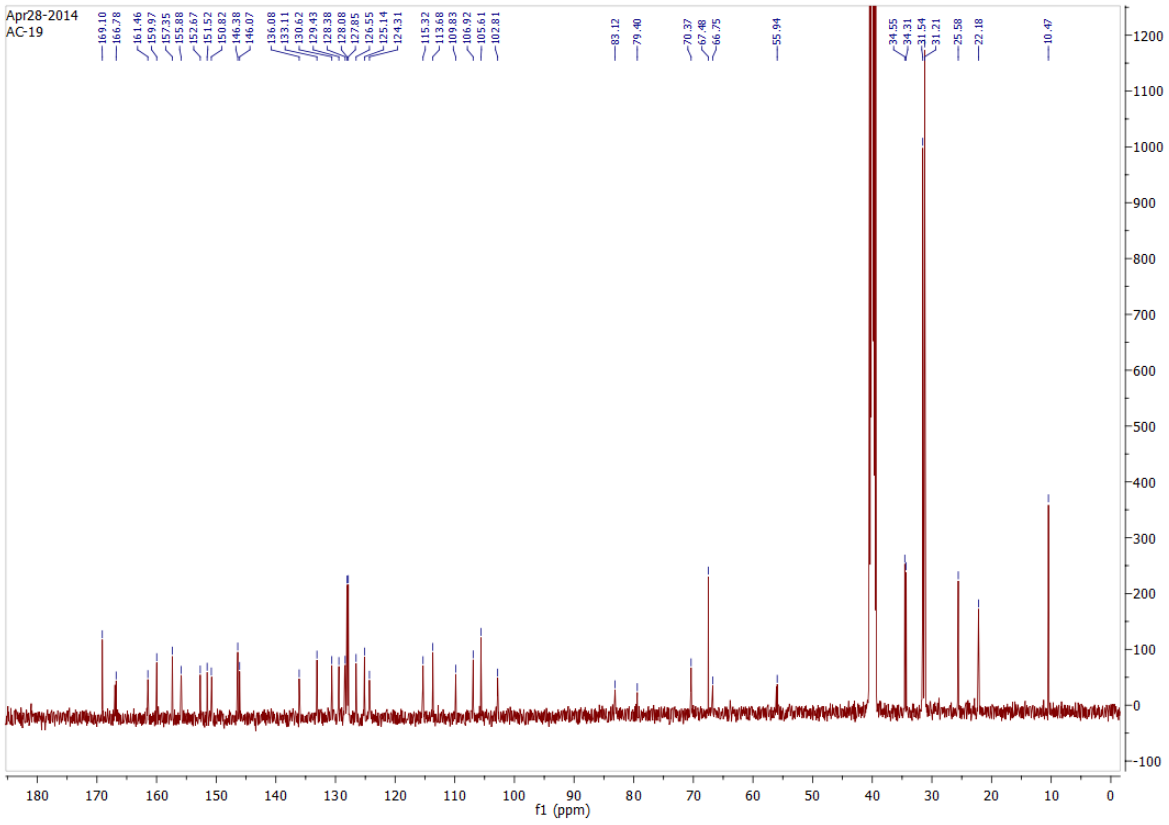


Synthetic Scheme

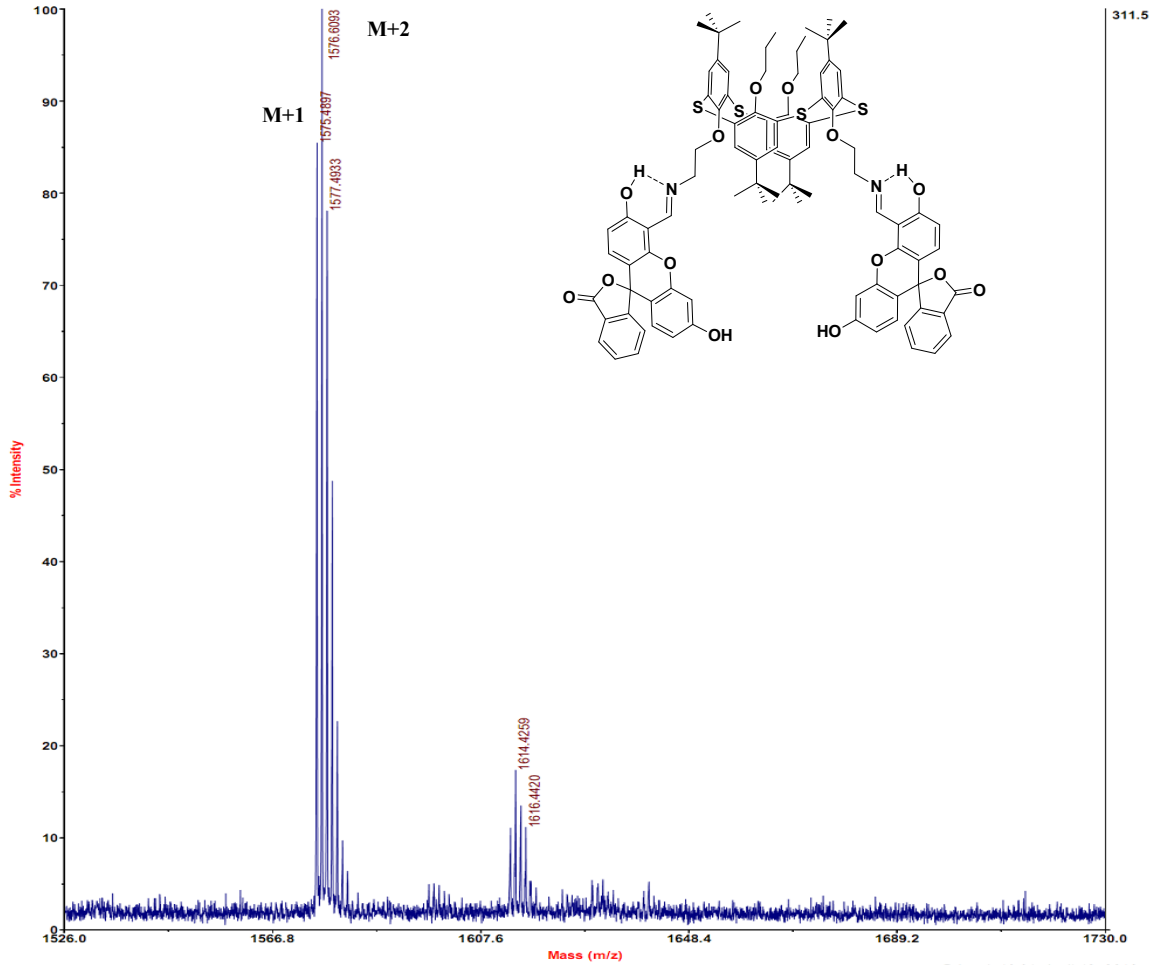
^{1}H NMR spectra of Compound **3** (DMSO-d_6, 500 MHz)



^{13}C NMR spectra of Compound **3** (DMSO-d_6, 500 MHz)



Mass spectra of Compound **3** (MALDI-TOF)



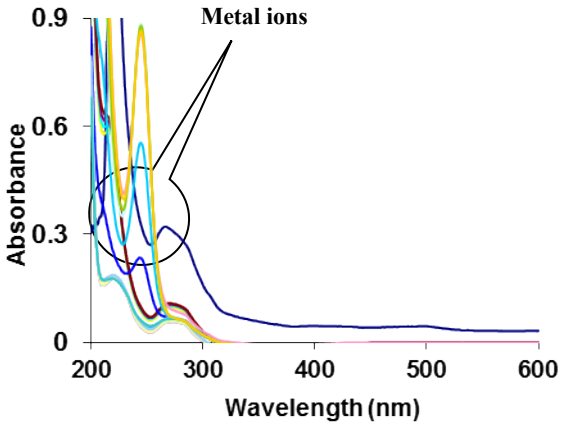


Figure 1. Absorption spectra of probe **3** (5.0 μM) upon addition of various cations: Cu^{2+}, Ag^{+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Na^{+}, K^{+}, Li^{+}, Mg^{2+}, Be^{2+}, Ca^{2+} (100 equiv) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0.

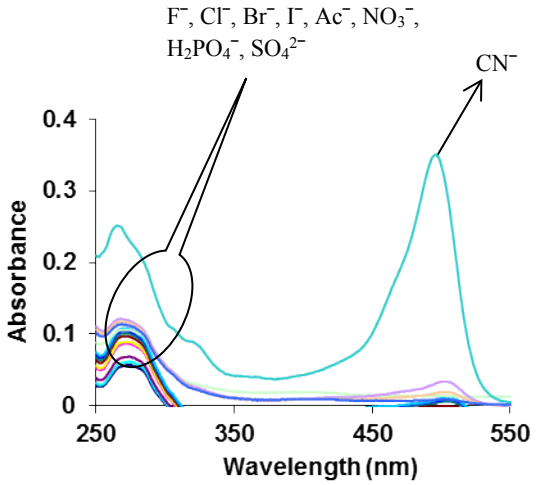


Figure 2. Absorption spectra of probe **3** (5.0 μM) upon addition of various different anions: F^-, Cl^-, Br^-, I^-, Ac^-, NO_3^-, $H_2PO_4^-$, SO_4^{2-}, CN^- (0-25 equiv) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0.

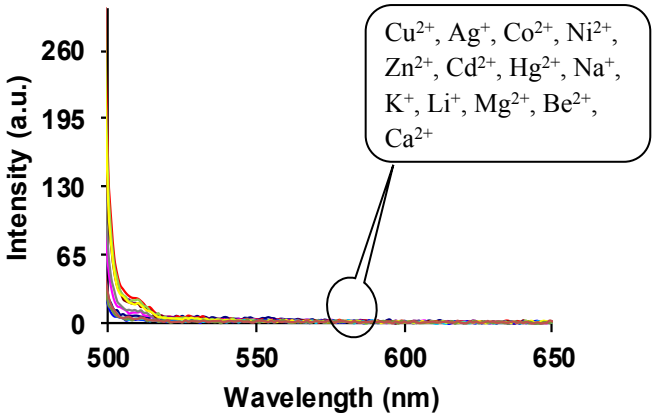


Figure 3. Fluorescence spectra of **3** (5.0 μM) upon addition of metal ions: Cu^{2+}, Ag^{+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Na^{+}, K^{+}, Li^{+}, Mg^{2+}, Be^{2+}, Ca^{2+} (100 equiv) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 490 nm.

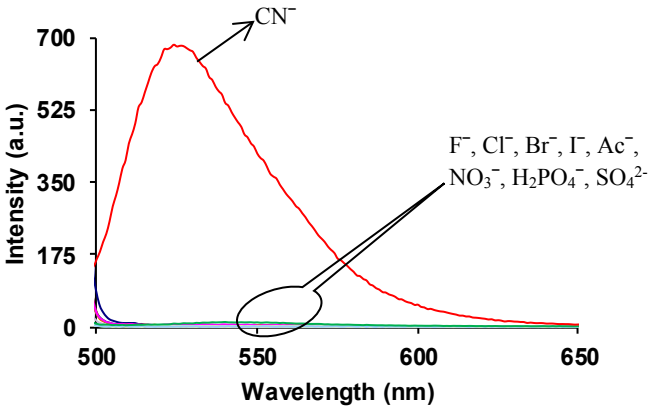
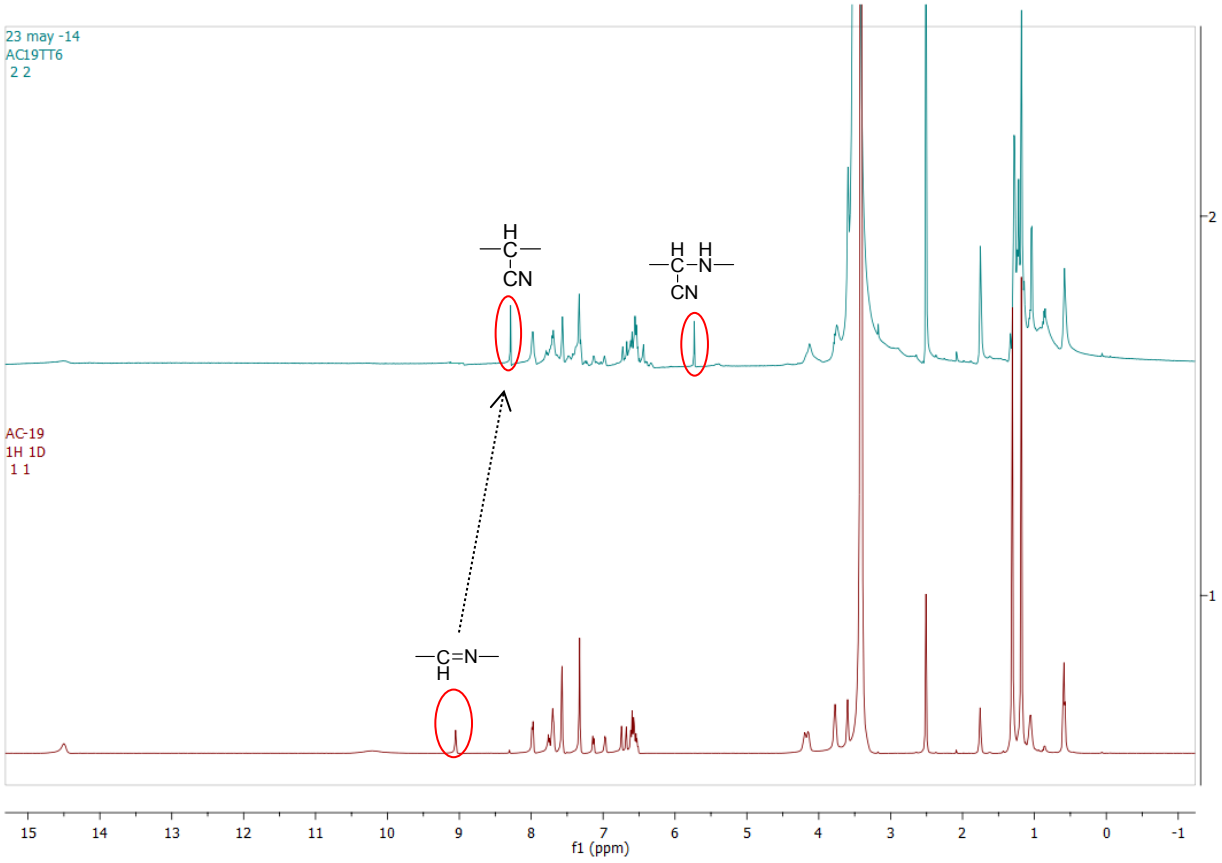
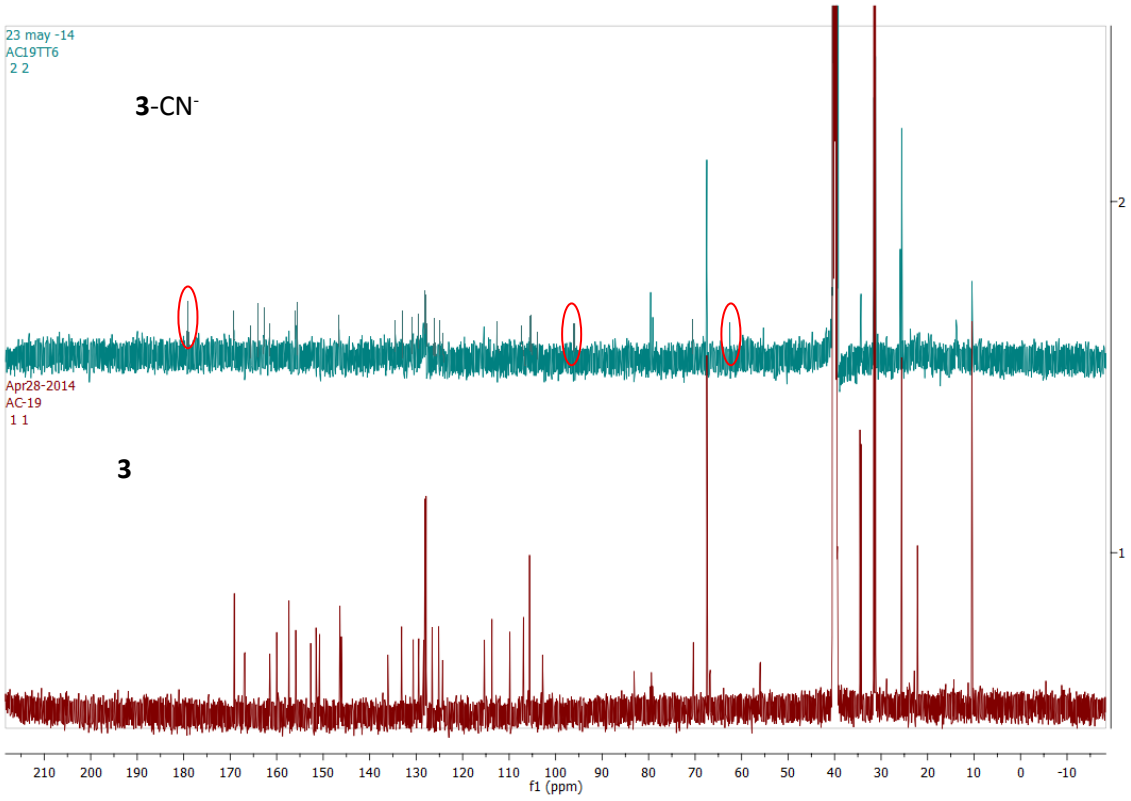


Figure 4. Fluorescence spectra of **3** (5.0 μM) upon addition of (0-25 equiv) of various different anions: F^-, Cl^-, Br^-, I^-, Ac^-, NO_3^-, $H_2PO_4^-$, CN^-, SO_4^{2-} in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 490 nm.

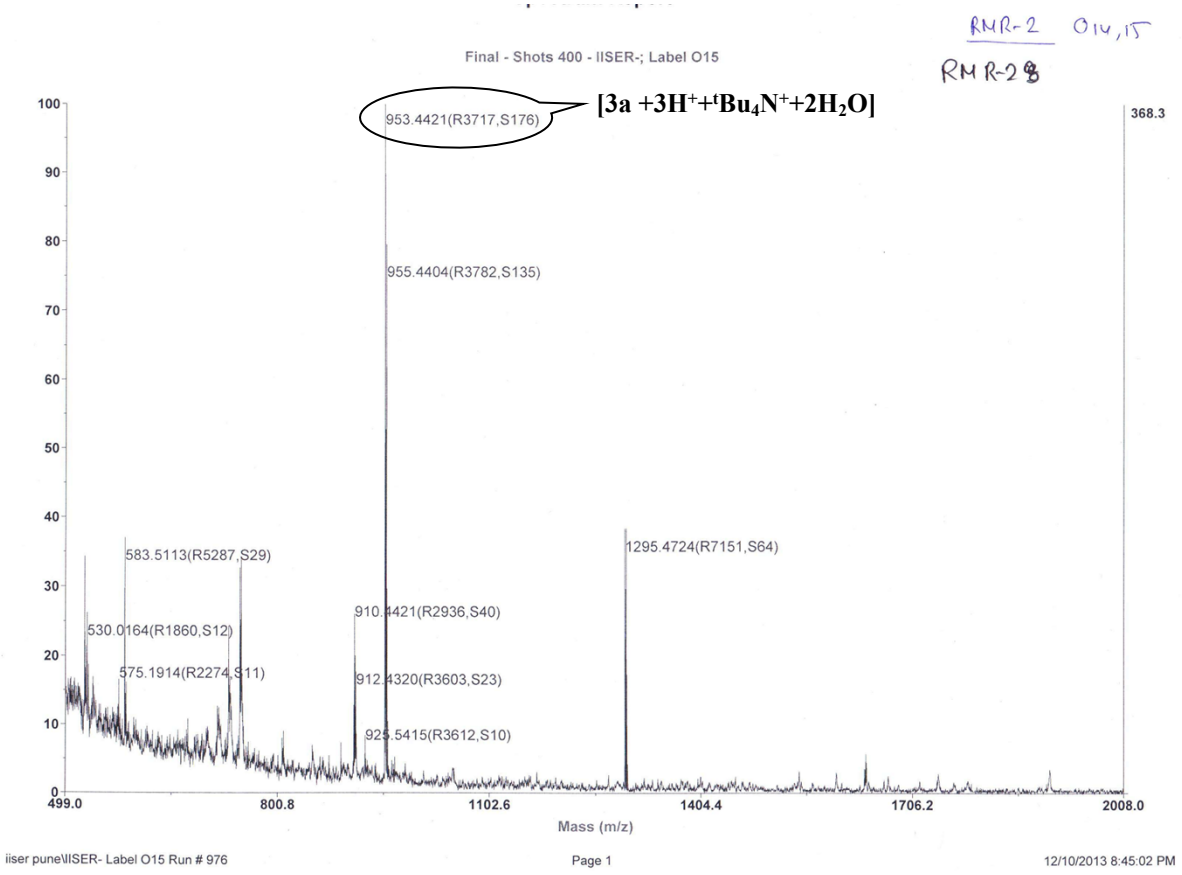
^{1}H NMR titration of compound **3** with CN^{-} (TBACN) (DMSO-d_6, 500 MHz)



^{13}C NMR of compound **3** and **3**a (cyanide adduct) (DMSO-d_6, 500 MHz)



Mass spectra of Cyanide –Adduct (MALDI-TOF)



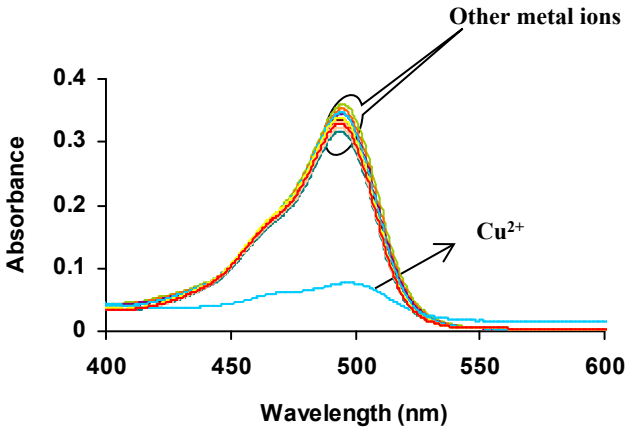


Figure 5. Absorption spectra of adduct **3a** upon addition of various different metal ions: Cu^{2+}, Ag^{+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Na^{+}, K^{+}, Li^{+}, Mg^{2+}, Be^{2+}, Ca^{2+} (0-44 equiv) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0.

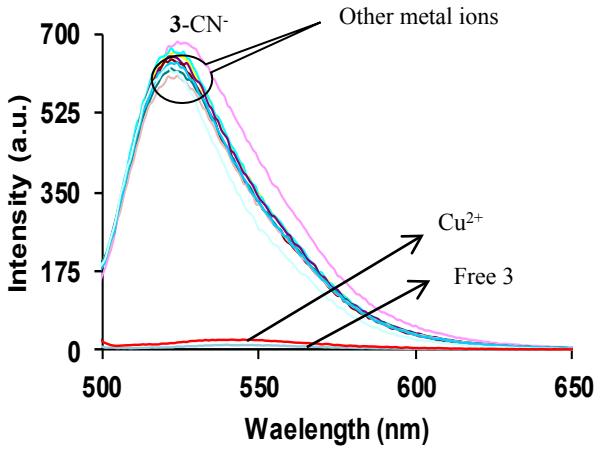


Figure 6. Fluorescence spectra of adduct **3a** (5.0 μM) in response to the addition of different metal ions (Cu^{2+}, Ag^{+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Na^{+}, K^{+}, Li^{+}, Mg^{2+}, Be^{2+}, Ca^{2+}) (44 equiv each) in CH_3CN/H_2O (8:2, v/v); λ_{ex} = 490 nm.

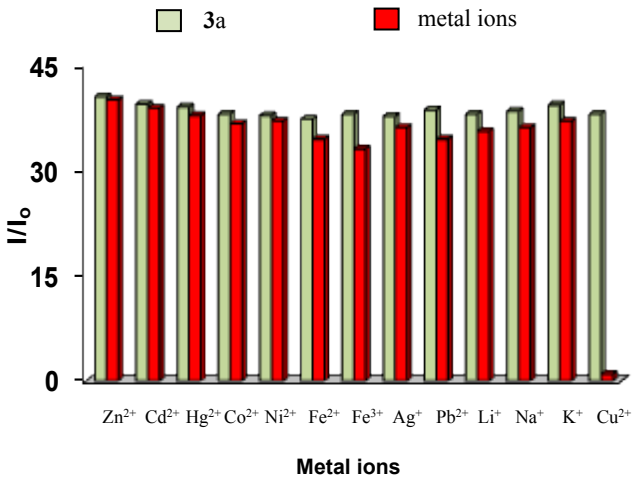
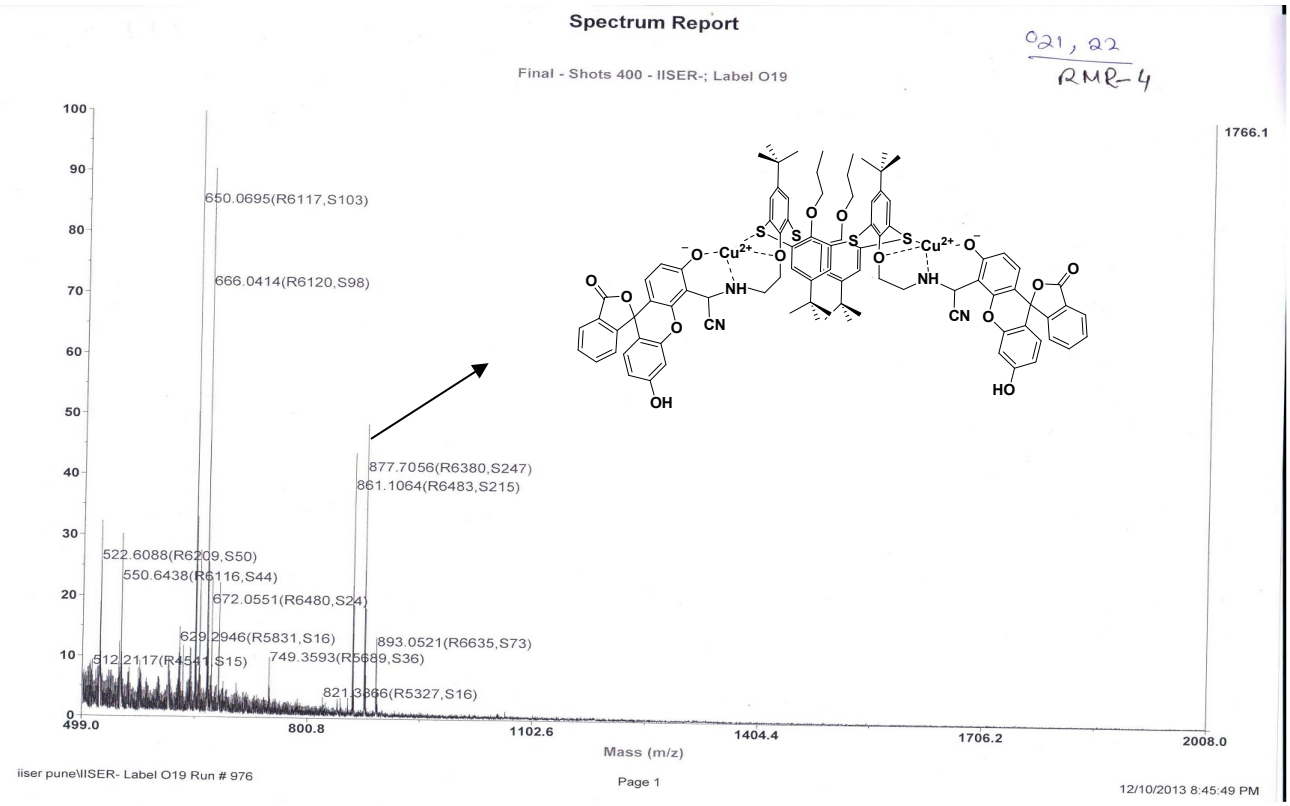


Figure 7. Fluorescence response of adduct **3a** towards various metal ions (44 equiv) in CH_3CN/H_2O (8:2, v/v); λ_{ex} = 490 nm. Bars represent the emission intensity ratio (I/I_0) (I_0 = initial fluorescence intensity at 528 nm; I = final fluorescence intensity at 528 nm after the addition of metal ions).

Mass analysis of Cyanide-adduct + Cu^{2+} complex (MALDI-TOF)



SPECFIT data of Cu^{2+} binding with 3a adduct

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Version = 3.0

[FILE]

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Date = 24-Oct-07

Time = 2:30:12 AM

Ncomp = 2

Nmeas = 44

Nwave = 321

[FACTOR ANALYSIS]

Tolerance = 1.000E-09

Max.Factors = 10

Num.Factors = 6

Significant = 3

Eigen Noise = 9.388E-01

Exp't Noise = 9.388E-01

#	Eigenvalue	Square Sum	Residual	Prediction
1	9.238E+07	1.565E+05	3.329E+00	Data Vector
2	1.343E+05	2.225E+04	1.255E+00	Data Vector
3	9.807E+03	1.245E+04	9.388E-01	Data Vector
4	2.675E+03	9.770E+03	8.318E-01	Probably Noise

5 1.469E+03 8.302E+03 7.668E-01 Probably Noise

6 5.998E+02 7.702E+03 7.386E-01 Probably Noise

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Time = 2:51:04 AM

Model = 0

Index = 3

Function = 1

Species = 3

Params = 3

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0 1 0	True	False	
2 1 0	True	False	

[SPECIES]	[FIXED]	[PARAMETER]		[ERROR]
1 0 0	True	0.00000E+00	+/-	0.00000E+00
0 1 0	True	0.00000E+00	+/-	0.00000E+00
2 1 0	False	9.58070E+00	+/-	5.03060E-02

[CONVERGENCE]

Iterations = 7

Convergence Limit = 1.000E-04

Convergence Found = 1.170E-05

Marquardt Parameter = 0.0

Sum(Y-y)^2 Residuals = 9.08231E+05

Std. Deviation of Fit(Y) = 8.01927E+00

[STATISTICS]

Experimental Noise = 9.388E-01

Relative Error Of Fit = 9.9564%

Durbin-Watson Factor = 0.3837

Goodness Of Fit, Chi^2 = 7.297E+01

Durbin-Watson Factor (raw data) = None

Goodness Of Fit, Chi^2 (raw data) = None

[COVARIANCE]

6.756E-03

[CORRELATION]

1.000E+00

[END FILE]

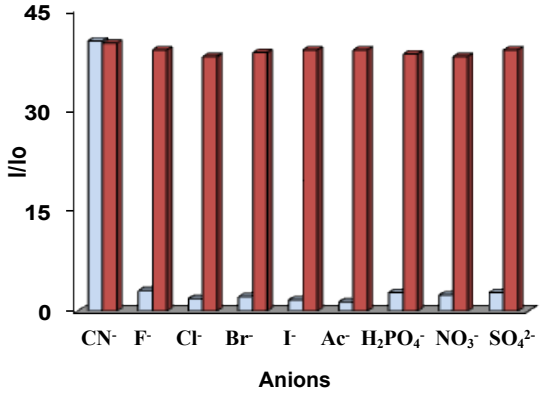


Figure 8. Fluorescence response of **3** (5.0 μM) to various anions (25 equiv) in CH_3CN/H_2O (8:2, v/v); λ_{ex} = 490 nm. Bars represent the emission intensity ratio (I/I_0) (I_0 = initial fluorescence intensity at 528 nm; I = final fluorescence intensity at 528 nm after the addition of anions). Blue bars represent selectivity (I/I_0) of **3** upon addition of different anions; red bars represent competitive selectivity of probe **3** towards CN^- ions (25 equiv) in the presence of other anions (25 equiv).

Calculations for detection limit:

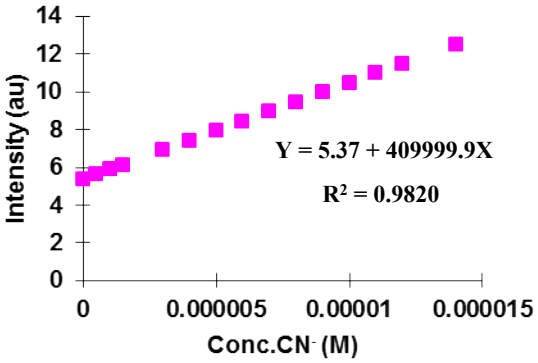


Figure 9. Figure showing the fluorescence intensity at 528 nm as a function of CN^- ions concentration (M).

The detection limit was calculated based on the fluorescence titration. To determine the S/N ratio, the emission intensity of receptor **3** without CN^- was measured by 10 times and the standard deviation of blank measurements was determined. The detection limit is then calculated with the following equation:

$DL = 3 \times SD/S$

Where SD is the standard deviation of the blank solution measured by 10 times; S is the slope of the calibration curve.

From the graph we get slope (S) = 409999.9, and SD value is 0.02612

Thus using the formula we get the Detection Limit (DL) = 1.911×10^{-7} M i.e. probe **3** can detect CN^- in this minimum concentration through fluorescence method.

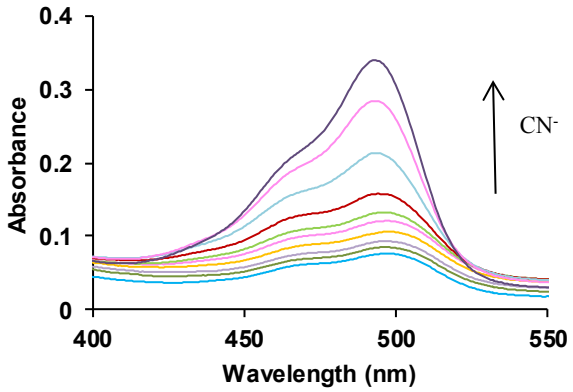


Figure 10. Absorption spectra of **3-CN$^-$-Cu^{2+}** upon the addition of CN^- ions (0-30 equiv) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0.

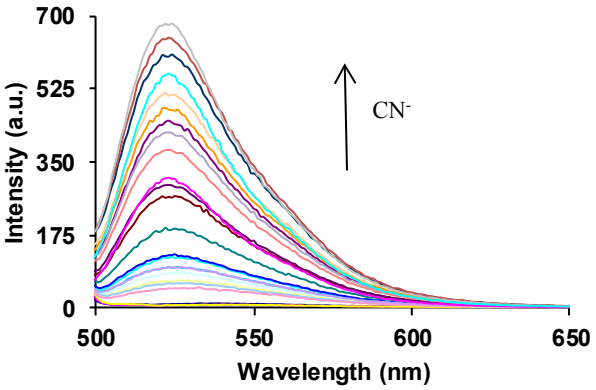


Figure 11. Fluorescence spectra of **3-CN$^-$-Cu^{2+}** upon the addition of CN^- anions (0-30 equiv) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 490 nm.

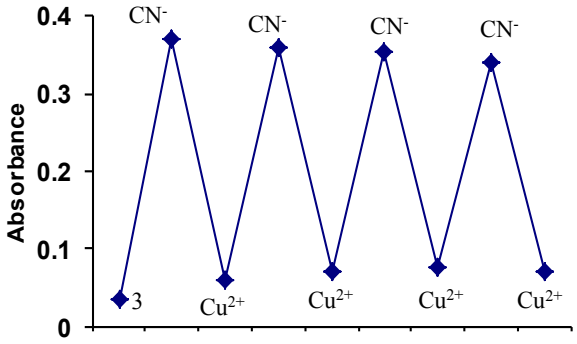
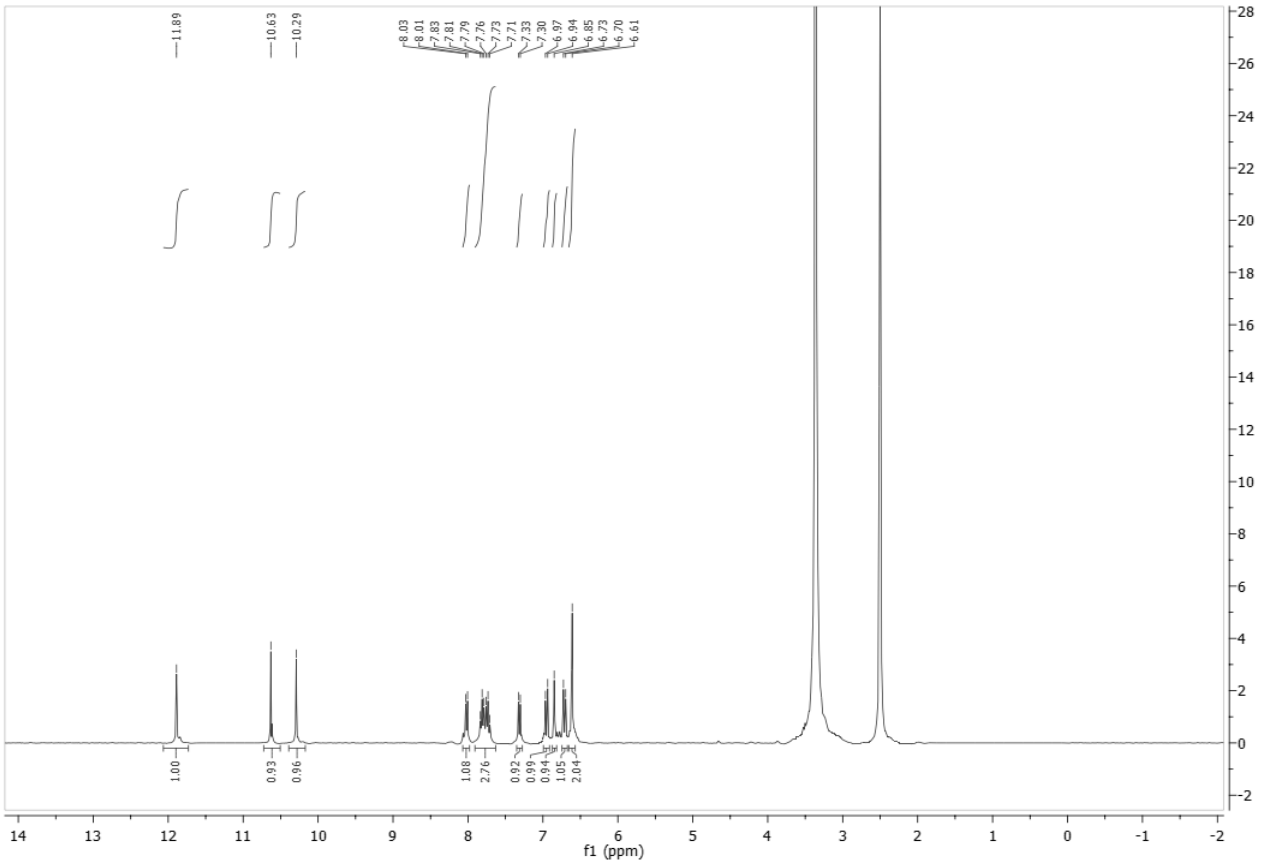


Figure 12. Reversibility changes in absorbance spectrum of compound **3** upon the sequential addition of CN^- and Cu^{2+} ions.

^{1}H NMR (DMSO-d_6, 400 MHz, ppm) of compound 2:



Mass spectrum of compound 2: