Supporting Information

Cu(II) Assisted Self-sorting Towards Pseudorotaxane Formation

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Materials and Methods

Materials: 1,3-Bis(aminomethyl)benzene, chloroacetylchloride, 4-hydroxybenzaldehyde, diethylenetriamine (DETA) were purchased from Sigma-Aldrich and used as received. Triethylamine and dichloromethane (DCM) were distilled over calcium hydride prior to use. Potasssium carbonate and sodium borohydride were purchased from Spectrochem, India. All solvents were procured from Merck.

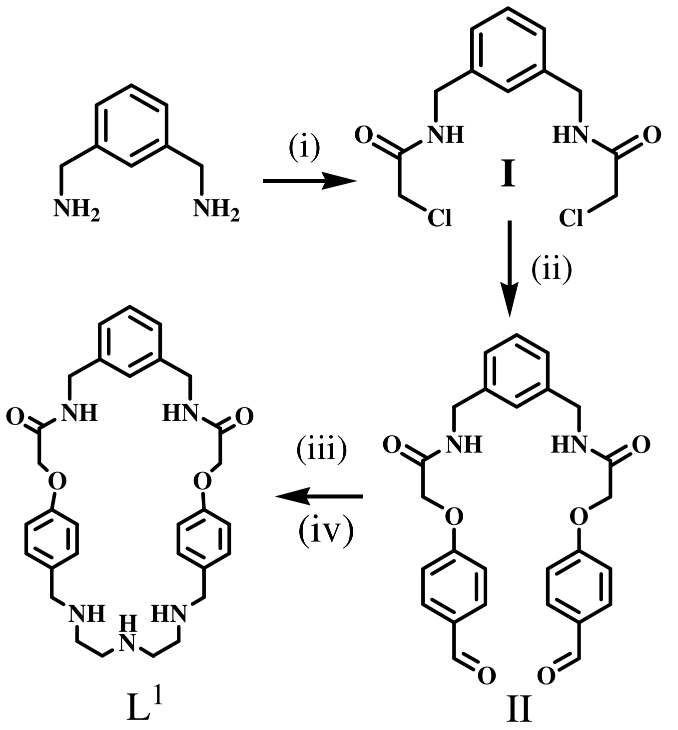
Methods: Melting points of **I**, **II**, **L^1** and complexes were determined on a BioCote melting point apparatus. Electrospray ionisation mass spectroscopy (ESI-MS) experiments were carried out on a Water's QtoF Model YA 263 spectrometer in positive ion ESI mode. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on 300 MHz and 75 MHz Bruker DPX-300 MHz NMR spectrometer and 500 MHz Bruker DPX-500 MHz spectrometer. Energy Dispersive X-ray (EDX) analyses were carried out on a field emission scanning electron microscope (FE-SEM) using JEOL, JSM-6700F equipment operated with the accelerating voltage 5 kV. The absorption spectra were recorded with a Perkin Elmer Lambda 950 UV-VIS-NIR scanning spectrophotometer at 298 K. EPR data were recorded on a JEOL JES-FA200 spectrometer with an X band micro web unit.

X-Ray crystallographic refinement details

X-ray Crystallography: Crystals suitable for single crystal X-ray diffraction studies were selected from the mother liquor and immersed in paratone oil and then mounted on the tip of a glass fibre and cemented using epoxy resin. Intensity data for the crystals **1**, and **2** were collected using MoK$_\alpha$ (λ = 0.7107 Å) radiation on a Bruker SMART APEX II diffractometer equipped with CCD area detector at 100 K. The data integration and reduction were processed with SAINT[1] software provided with the software package of SAMRT APEX II. An empirical absorption correction was applied to the collected reflections with SADABS[2]. The structures were solved by direct methods using SHELXTL[3] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97[4] program package. Graphics were generated using PLATON[5] and MERCURY 1.4.[6] the non-hydrogen atoms were refined anisotropically till convergence. In cases of complexes **1** and **2**, the hydrogen atoms were geometrically fixed at idealized positions. In cases of complexes **1**, and **2**, even though the data was collected at 100 K, the hydrogen atoms attached to the lattice water molecule could not be located from the difference Fourier map.

We tried to grow crystals of complex **1** from acetonitrile solution in different conditions (dilution, low temperature evaporation, slow evaporation at room temperature etc) to get better quality crystals to overcome the poor resolution of the data. Here we have presented the best set of data for **1** we obtained from different crystallization conditions whereas we were unsuccessful to get crystals from other solvents. CCDC-783143 (**1**) and CCDC-783144 (**2**) contain the supplementary crystallographic data for this paper. The diethylene triamine moiety of complex **2** was disordered at two sites and the occupancy factors were refined using the FVAR command of the SHELXTL program and isotropically refined. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Scheme 1S: Synthetic route for preparation of receptor $\mathbf{L^1}$



(i) DCM, chloroacetyl chloride, triethylamine, RT, 6h
(ii) K_2CO_3, acetone, 4-hydroxybenzaldehyde, 12h, reflux
(iii) MeOH-DCM, diethylenetriamine, RT, 12h
(iv) $NaBH_4$, 3h

Synthetic procedures for I, II and L^1

Synthesis of Compound **I**: In a 250 ml two neck round bottomed flask, 1,3 diaminometylbenzene (22 mmol, 3ml) was dissolved in 150 ml of dry dichloromethane. About 7.6 mL (55 mmol) of dry triethylamine was added. The mixture was allowed to stir at 0^0 C temperature in nitrogen atmosphere for 15 min. 4.3 mL (55 mmol) of chloroacetyl chloride was dissolved in another 50 mL of dry DCM and taken in a 100 mL pressure equalizing funnel. This solution was added dropwise for a period of 1 hour at constant stirring 0^o C temperature. After the addition, the reaction mixture was allowed to stir at room temperature in nitrogen atmosphere for another 6 h. The white precipitate (triethylammonium chloride) was filtered, and washed three times with cold DCM. The filtrate was collected and washed with 2M HCl, saturated $NaHCO_3$ solution and saturated NaCl solution. The organic phase was separated, and dried over anhydrous sodium sulfate. Then the solvent was evaporated in *vacuo* to yield the desired product **I** as yellowish solid. (4.5 g, 82%). M P: 147-148ºC. HRMS (ESI): m/z calcd. for $C_{12}H_{14}Cl_2N_2O_2Na$ [M + Na]$^+$, 311.0330, found 311.0330, error 0.0 ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.09 (s, dH, -C*H*$_2$Cl), 4.48 (d, 4H, Ar-C*H*$_2$, J = 5 Hz), 6.94 (br, 2H, -N*H*), 7.20-7.36 (m, 4H, Ar-*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 42.74 (-*C*H$_2$Cl), 43.74 (Ar-*C*H$_2$), 127.20 (Ar-*C*), 127.27 (Ar-*C*), 129.48 (Ar-*C*), 138.17 (Ar-*C*), 166.11 (-*C*=O).

Synthesis of Compound **II**: In a 250 ml round bottomed flask 2.9 g (10 mmol) of **I** was dissolved in 100 ml of acetone. 4.1g (30 mmol) of K_2CO_3, 2.6 g (22 mmol) of 4-hydroxybenzaldehyde were added to that solution at room temperature.The reaction mixture was allowed to stir at 80^o C in nitrogen atmosphere for 12 h. The off white precipitate was filtered and repeatedly washed with acetone and water. This off white solid, compound **II** (75%) was dried and can be used in the next step without further purification. M P: 197-198ºC. HRMS (ESI): m/z calcd. for $C_{26}H_{24}N_2O_6Na$ [M+Na]$^+$, 483.1532, found 483.1531, error 0.2 ppm. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.53 (d, 4H,Ar-CH$_2$, J = 6 Hz), 4.63 (s, 4H, -COCH$_2$), 6.84 (br, -N*H*, 2H), 7.04 (d, 2H, Ar-H, J = 9 Hz), 7.21 – 7.33 (m, 3H, Ar-*H*), 7.87 (d, 4H, Ar-H, J = 9.0 Hz), 9.92 (s, -C*H*O). ^{13}C NMR (125 MHz, $CDCl_3$): δ 42.91 (Ar-*C*H$_2$), 67.37 (-CO*C*H$_2$), 115.04 (Ar-*C*), 127.08 (Ar-*C*), 127.15 (Ar-*C*), 129.33 (Ar-*C*), 131.26 (Ar-*C*), 132.12 (Ar-*C*), 138.31 (Ar-*C*) 161.69 (Ar-*C*), 167.16 (-*C*O), 190.49(-*C*HO).

Synthesis of macrocycle **L^1**: In a 500ml three neck round bottom flask, two were fitted with 100ml pressure equalizer and another for nitrogen atmosphere. Compound **II,** 460 mg (0.1 mmol) in 50 ml DCM in a pressure equalizer and diethylenetriamine 0.1 ml (0.1 mmol) dissolved in 50 ml of DCM in another pressure equalizer, were added drop by drop to the stirring 100 ml methanol solvent. After complete addition the reaction mixture was stirred for 12h. Sodium borohydride 76 mg (2 mmol) was added to the reaction mixture and stirred for 3h. The reaction mixture was filtered and the filtrate was evaporated. The solid was dissolved in 100 ml of DCM and was washed with water and brine solution.

The organic phase was separated, and dried over anhydrous sodium sulfate. The solvent was evaporated in *vacuo* to yield the desired product **L**^{1} as white solid. (435 mg, 81%). M P: 172-173°C. HRMS (ESI): m/z calcd. for $C_{30}H_{38}N_5O_4$ [M + H]$^{+}$, 532.2924, found 532.2923, error 0.2 ppm. ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.75 (m, NHC*H$_2$*C*H$_2$*, 8H), 3.70 (s, -COC*H$_2$*O-, 4H), 4.53 (m, Ar-C*H$_2$*, 8H), 6.78 (d, Ar-*H*, J = 8.7 Hz), 7.20 (d, Ar-*H*, J =8.7 Hz, 4H), 7.24-7.32 (m, Ar-*H*, 3H). ^{13}C NMR (75.47 MHz, CDCl$_3$): δ 42.99 (CH_2NH_2), 48.67 (CH_2NH_2), 48.95 (Ar-*C*H$_2$NH), 53.31 (Ar-*C*H$_2$NH), 67.43 (OCH_2), 114.61 (Ar-*C*), 127.93 (Ar-*C*), 129.66 (Ar-*C*), 134.56 (Ar-*C*), 138.69 (Ar-*C*),156.11 (Ar-*C*), 168.08 (*C*O) .

Synthesis of Complex **1**:

L^{1} (0.1 mmol, 53.2 mg) was dissolved in 10 ml of MeOH/CH_2Cl_2 (1:1); Cu $(ClO_4)_2$ (0.1 mmol, 37mg) was added to the stirring solution. The reaction mixture was stirred for another 4h. A precipitate developed which was filtered and collected after repeated washing with methanol. Characterized by ESI mass spectroscopy. Yield 84%

Syntheses of Complexes **2-5**:

A solution of $Cu(ClO_4)_2$ (0.1 mmol, 37 mg) in MeOH (5 mL) was added to a solution of macrocycle **L**^{1} (0.1 mmol, 53.2 mg) in CH_2Cl_2 (5 mL) at room temperature. The bidentate ligand (**L**^{2}**/ L**^{3}**/ L**^{4}**/ L**^{5}, each of 0.1 mmol for complexes **2-5** respectively) was added to the mixture. The resultant mixture was stirred for 4 h and the precipitate was collected by filtration and also characterized by ESI mass spectroscopy. Yield 78-85%

Complexation by path a:

A solution of $Cu(ClO_4)_2$ (0.1 mmol, 37 mg) in MeOH (5 mL) was added to a solution of macrocycle **L**^{1} (0.1 mmol, 53.2 mg) in CH_2Cl_2 (5 mL) at room temperature. After 10 minutes, a mixture of bidentate ligands (**L**^{2}**, L**^{3}**, L**^{4}, and **L**^{5} each of 0.1 mmol) in 5 ml CH_2Cl_2 was added to the solution. The mixture was stirred for 4 h. Then precipitate was collected by filtration, dried and characterized by ESI mass spectroscopy. Yield 81%

Complexation by path b:

L^{1} (0.1 mmol, 53.2 mg) and **L**^{2} (0.1 mmol,) were dissolved in 10 ml CH_2Cl_2 and stirred for 5 minutes, then a solution of divalent metal perchlorates (0.1 mmol of each) of Co, Ni, Cu, Zn dissolved in MeOH (10 ml) was poured into the stirring solution at room temp. After 4 hr a bluish precipitate developed which was collected by filtration and repeatedly washed with MeOH to remove un-reacted components. The precipitate was collected by filtration, dried and characterized by ESI mass spectroscopy and energy dispersion X-ray (EDX) studies. Yield 83%

Complexation upon mixing of metals Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and **L**^{1}-**L**^{5}:

In a (0.1 mmol, 53.2 mg) solution of **L**^{1} in 10 ml CH_2Cl_2, a mixture of bivalent metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} each of 0.1 mmol) in 5 ml MeOH was added and stirred for 10 minutes. A mixture of bidentate ligands (**L**^{2}**, L**^{3}**, L**^{4}, and **L**^{5} each of 0.1 mmol) in 5 ml MeOH was poured into the above stirring solution.

After 4h the precipitate was filtered and repeatedly washed with MeOH, dried in vacuum and characterised by ESI mass spectroscopy. Yield: 82%

Solution state selectivity study

We prepared the standard stock solutions of $\mathbf{L^1}$ ($4x10^{-3}$M), $\mathbf{L^2}$ ($4x10^{-3}$M), Cu^{2+} ($4x10^{-3}$M), a mixture of $\mathbf{L^2}$-$\mathbf{L^5}$ ($4x10^{-3}$M, each), a mixture of Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} ($4x10^{-3}$M, each) in methanol.

i) For path-a, Scheme 1, $\mathbf{L^1}$ ($4x10^{-3}$M) and Cu^{2+} ($4x10^{-3}$M) each of 50 μL were added in a glass vial and then a solution containing $\mathbf{L^2}$-$\mathbf{L^5}$ ($4x10^{-3}$M, each) 50 μL was added to the above mixture. The resulted clear solution was subjected for ESI-MS which showed the ternary complex peak corresponds to $[L^1.L^2.Cu.ClO_4]^+$(Figure 18S).

ii) For path b, scheme 1, 50 μL of $\mathbf{L^1}$ ($4x10^{-3}$M) and 50 μL of solution containing mixtures of Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} ($4x10^{-3}$M, each) were mixed in a glass vial and then 50 μL of $\mathbf{L^2}$ ($4x10^{-3}$M) was added to the above mixture. The resulted clear solution was subjected for ESI-MS which showed the ternary complex peak corresponds to $[\mathbf{L^1}.\mathbf{L^2}.Cu.ClO_4]^+$(Figure 19S).

iii) In this case, 50 μL of $\mathbf{L^1}$($4x10^{-3}$M) and 50μL of solution containing mixtures of Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} ($4x10^{-3}$M, each) were added in a glass vial and then a solution of $\mathbf{L^2}$-$\mathbf{L^5}$ ($4x10^{-3}$M, each) 50 μL was added to the above mixture . The resulted clear solution was subjected for ESI-MS which showed the ternary complex peak corresponds to $[\mathbf{L^1}.\mathbf{L^2}.Cu.ClO_4]^+$ (Figure 20S).

Figure 1S. ESI-MS of compound **I**

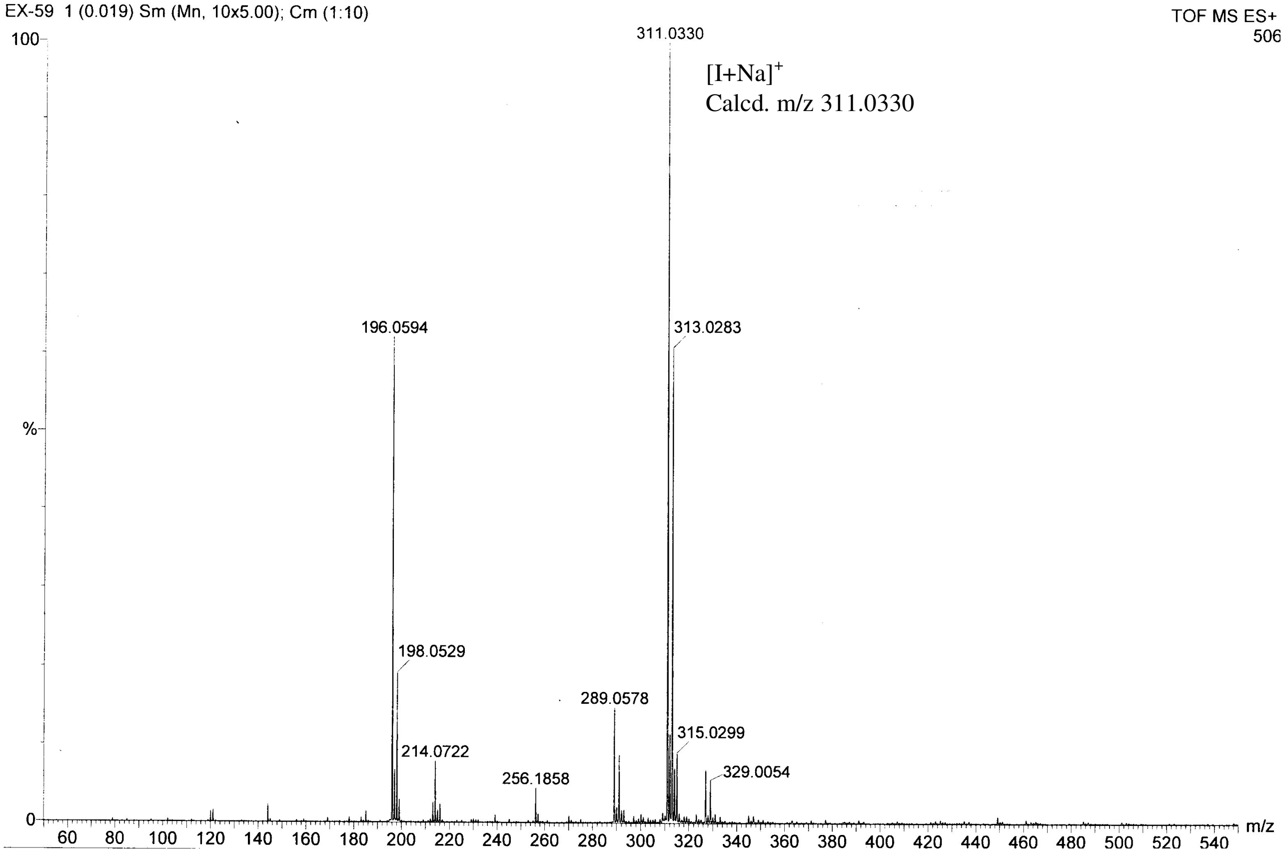


Figure 2S. 300 MHz ^{1}H-NMR spectrum of compound **I** in $CDCl_3$ at 25ºC.

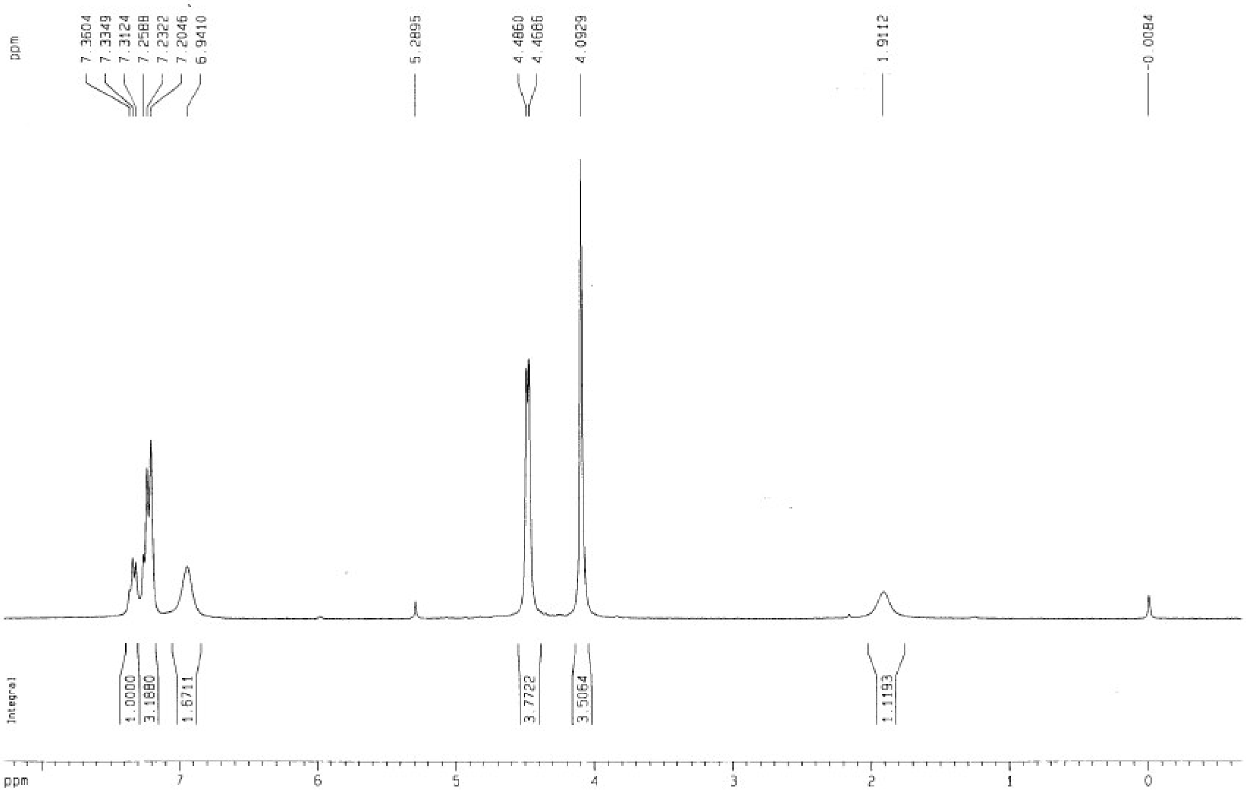
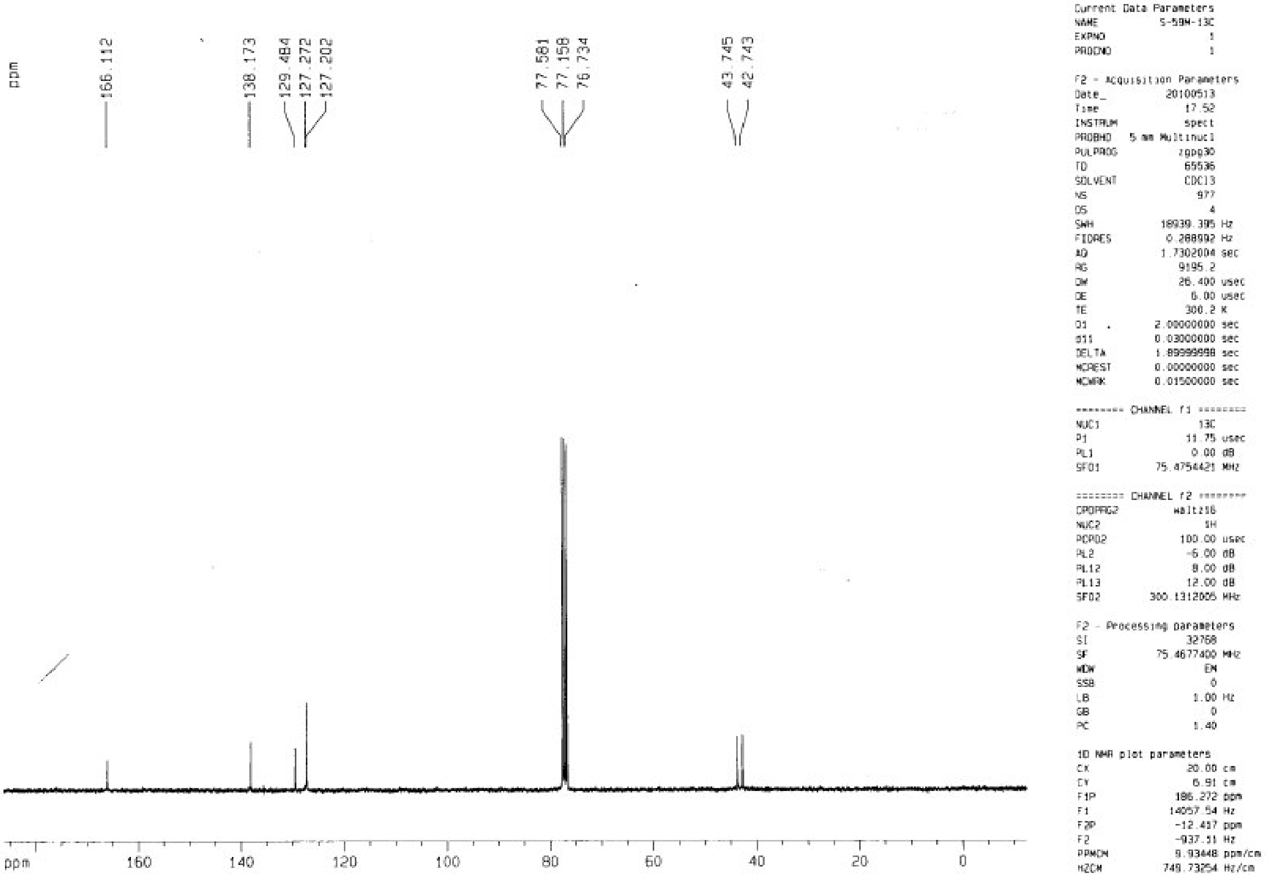


Figure 3S.300 MHz ^{13}C-NMR spectrum of compound **I** in $CDCl_3$ at 25ºC.



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PL13               12.00 dB
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Figure 4S. ESI-MS of compound **II**

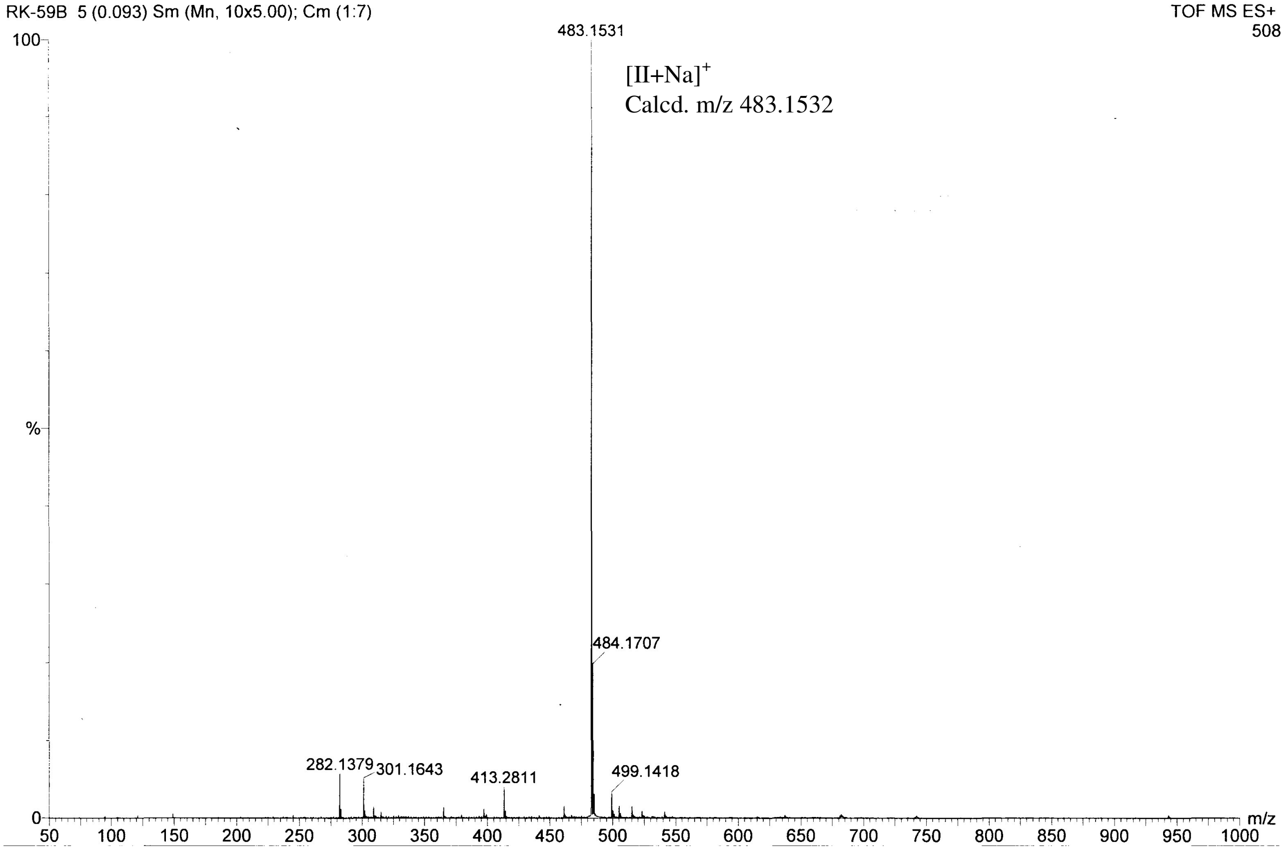

Figure 5S. 500 MHz ^{1}H-NMR spectrum of compound **II** in $CDCl_3$ at 25ºC.

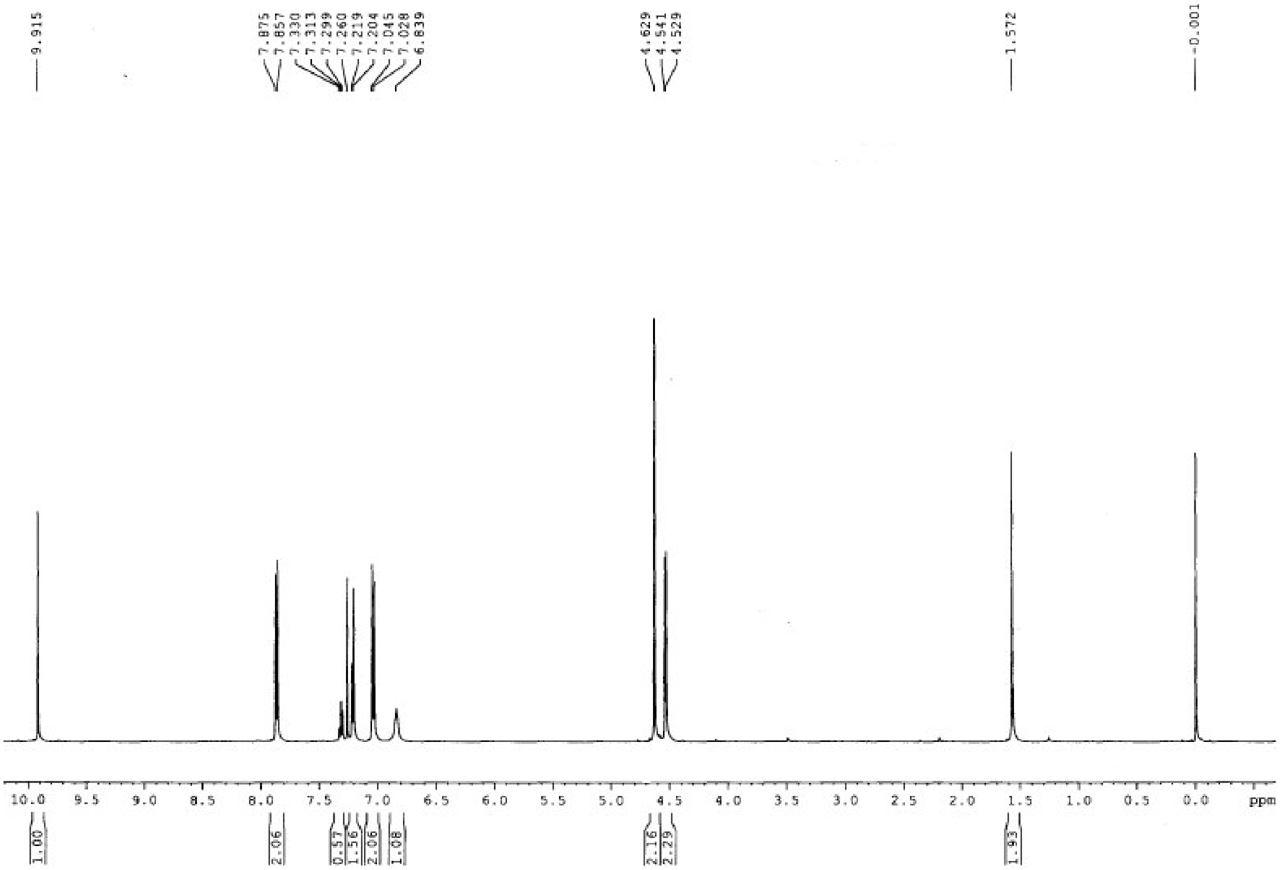

Figure 6S. 500 MHz ^{13}C-NMR spectrum of compound **II** in $CDCl_3$ at 25ºC.

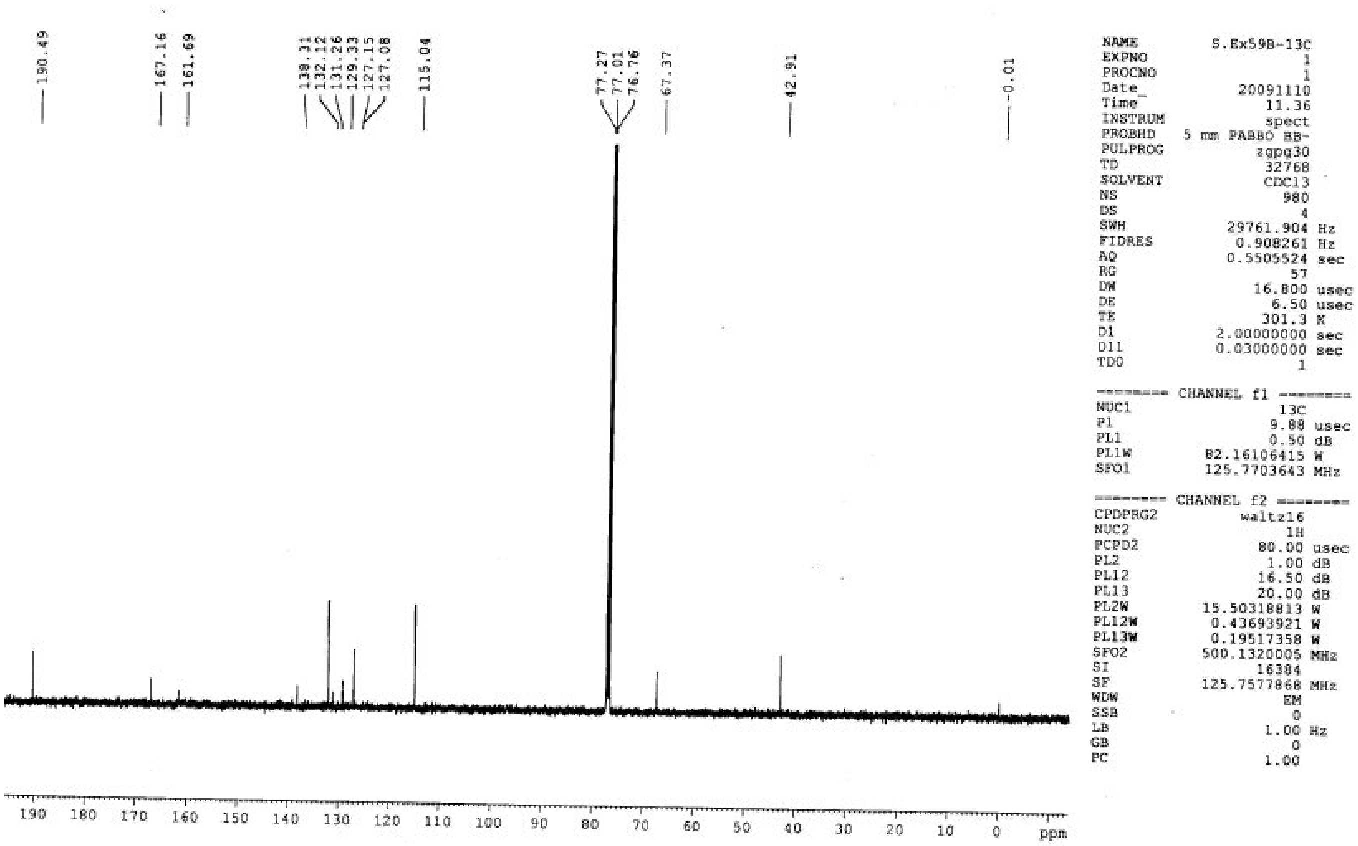

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Figure 7S. ESI-MS of **L**^{1}

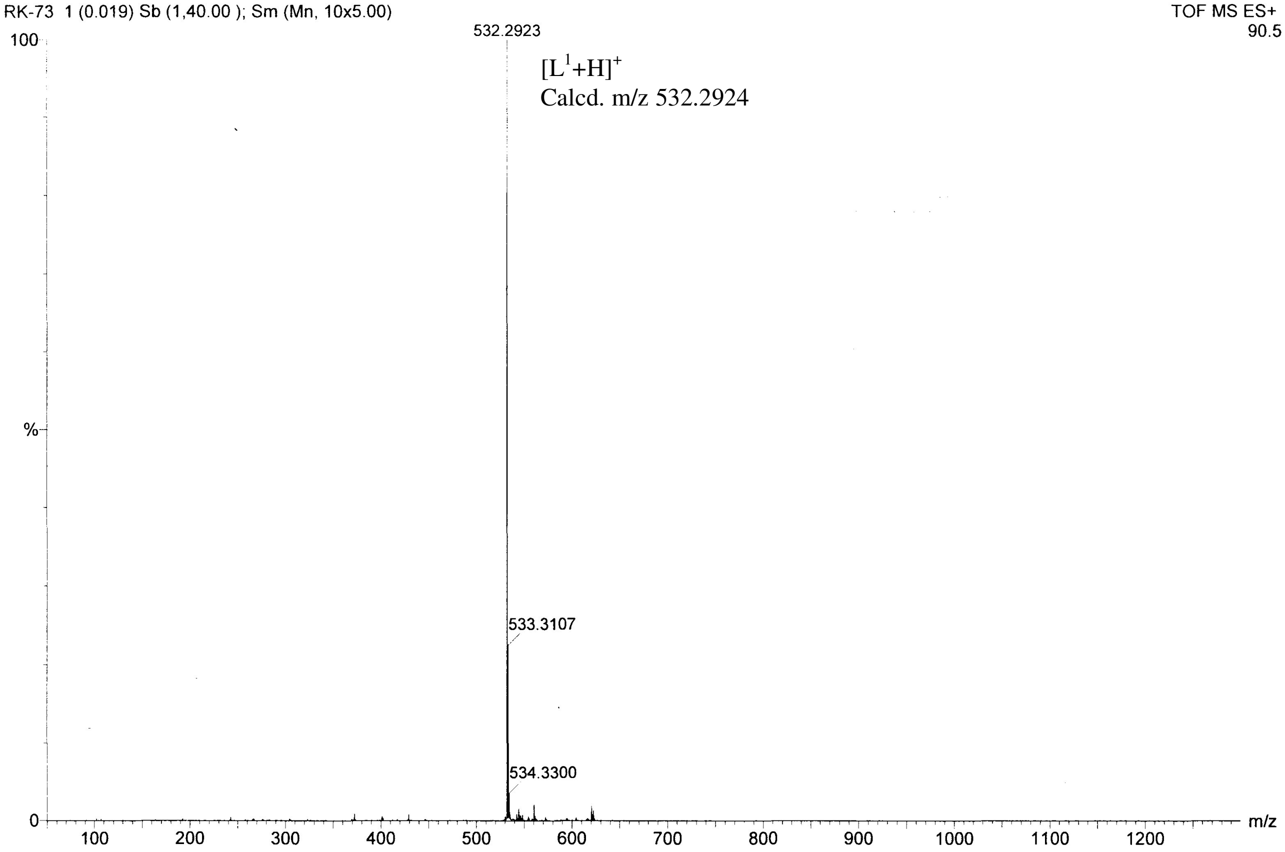


Figure 8S. 300 MHz ^{1}H-NMR spectrum of **L^1** in $CDCl_3$ at 25ºC.

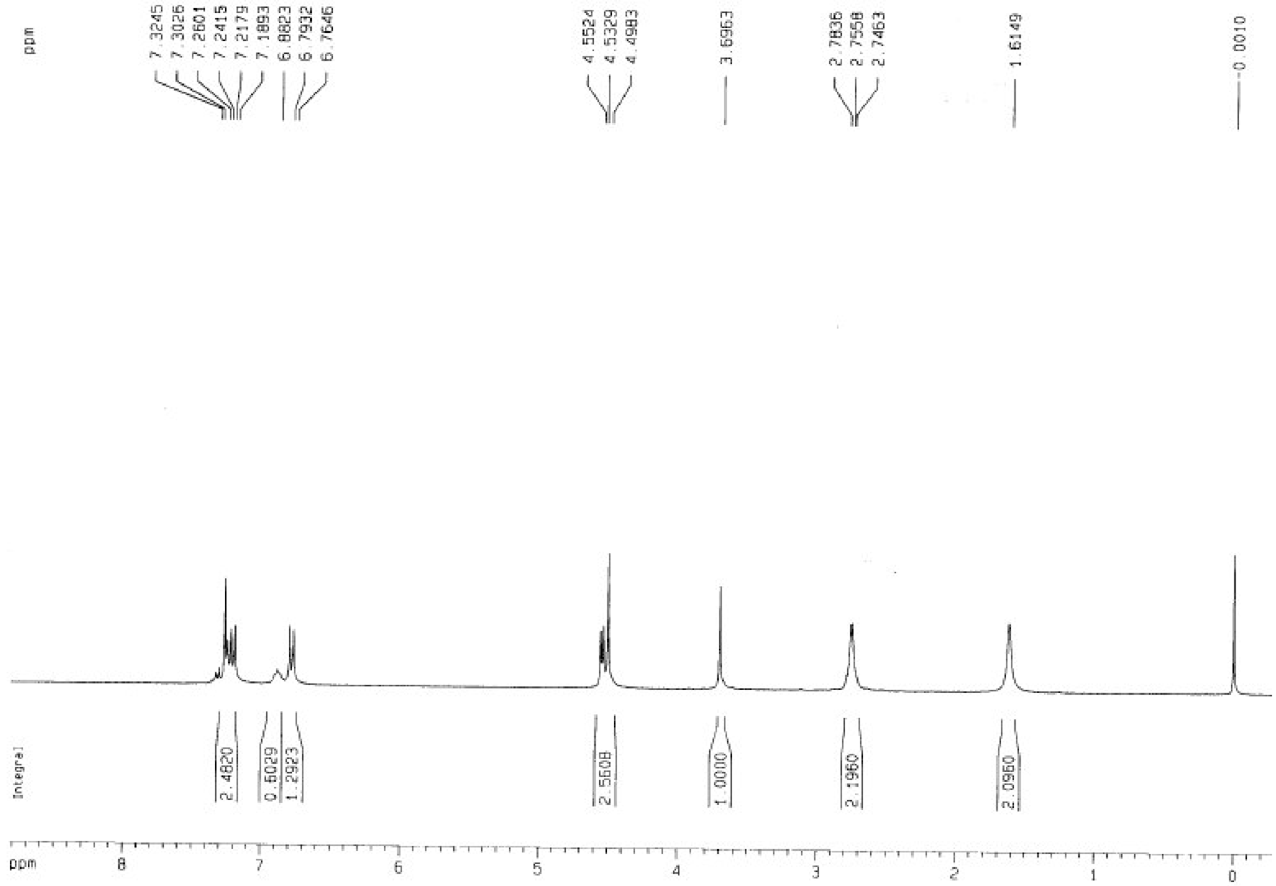
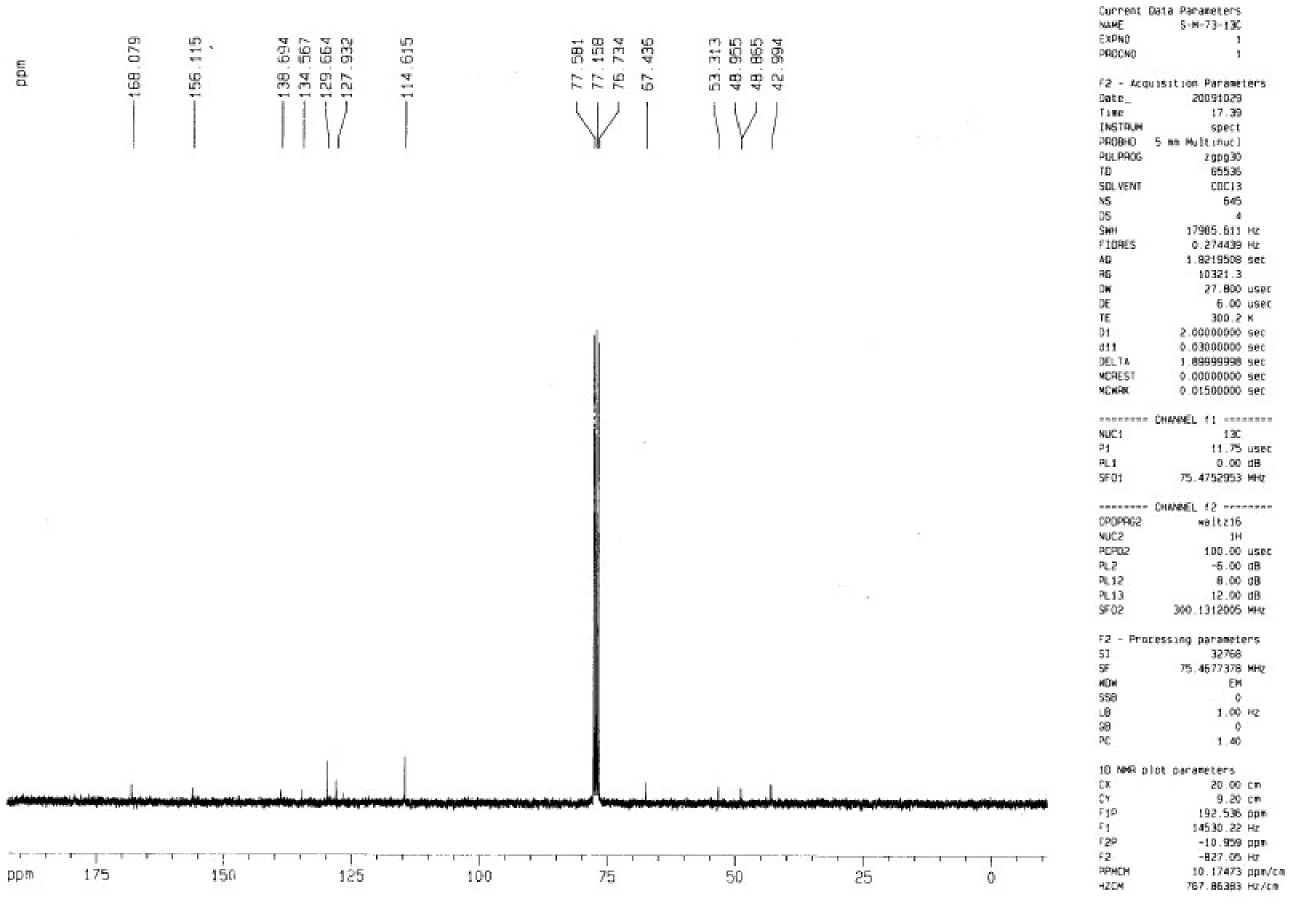


Figure 9S. 300 MHz ^{13}C-NMR spectrum of **L^1** in $CDCl_3$ at 25ºC.



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MCWRK         0.01500000 sec

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P1                 11.75 usec
PL1                 0.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
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NUC2                  1H
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PL12                8.00 dB
PL13               12.00 dB
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F2 - Processing parameters
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F2P              -10.959 ppm
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Figure 10S. ESI-MS of complex **1**

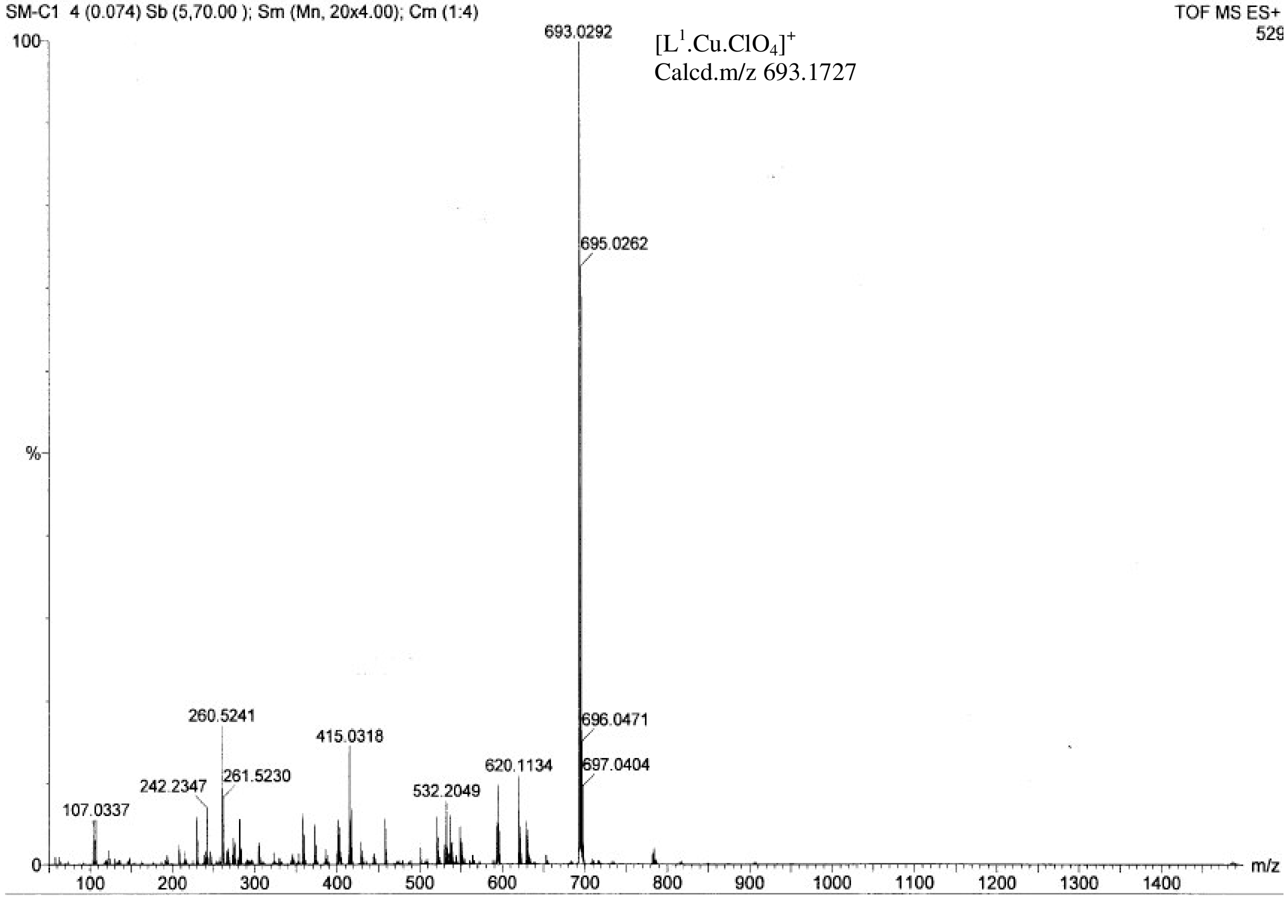

$[L^1.Cu.ClO_4]^+$
Calcd.m/z 693.1727

Figure 11S. UV/Vis titration of **L^1** (5 x 10^{-3} M) and Cu^{2+}(9.9 x 10^{-3}M) in methanol

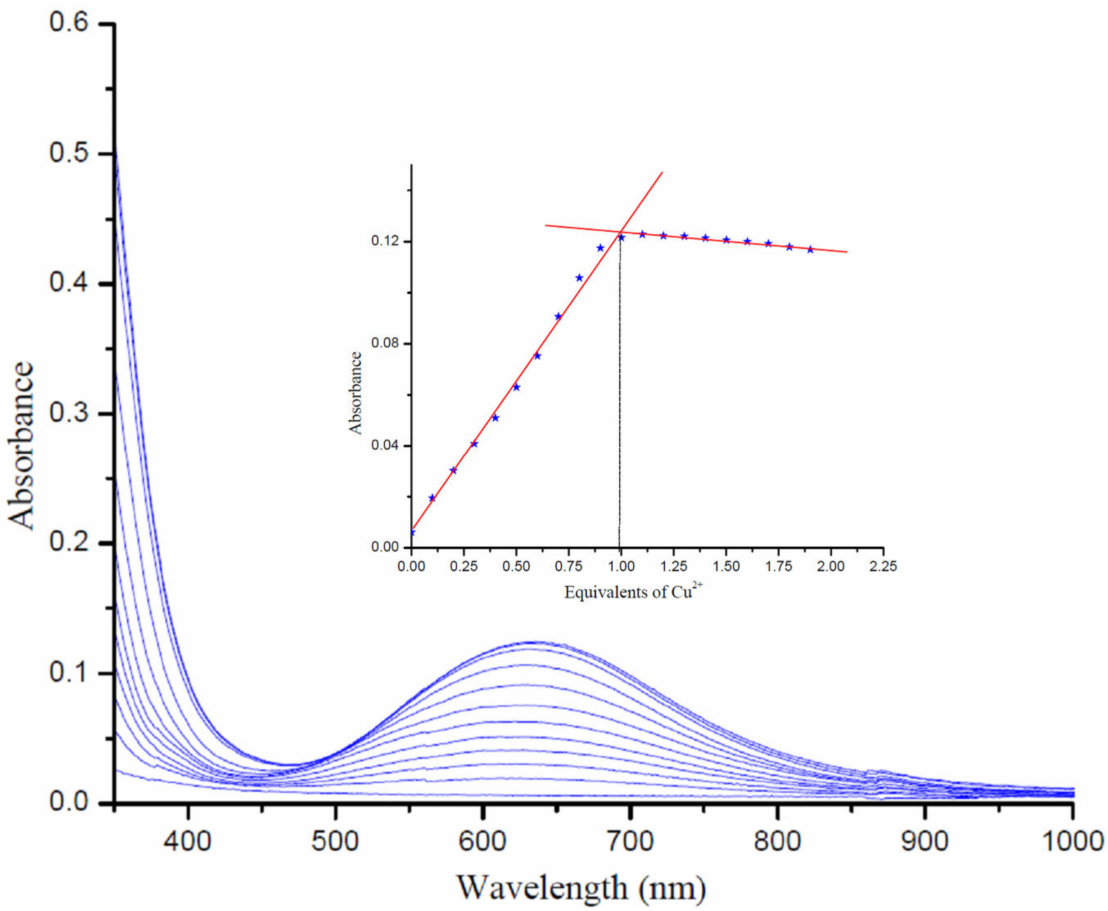
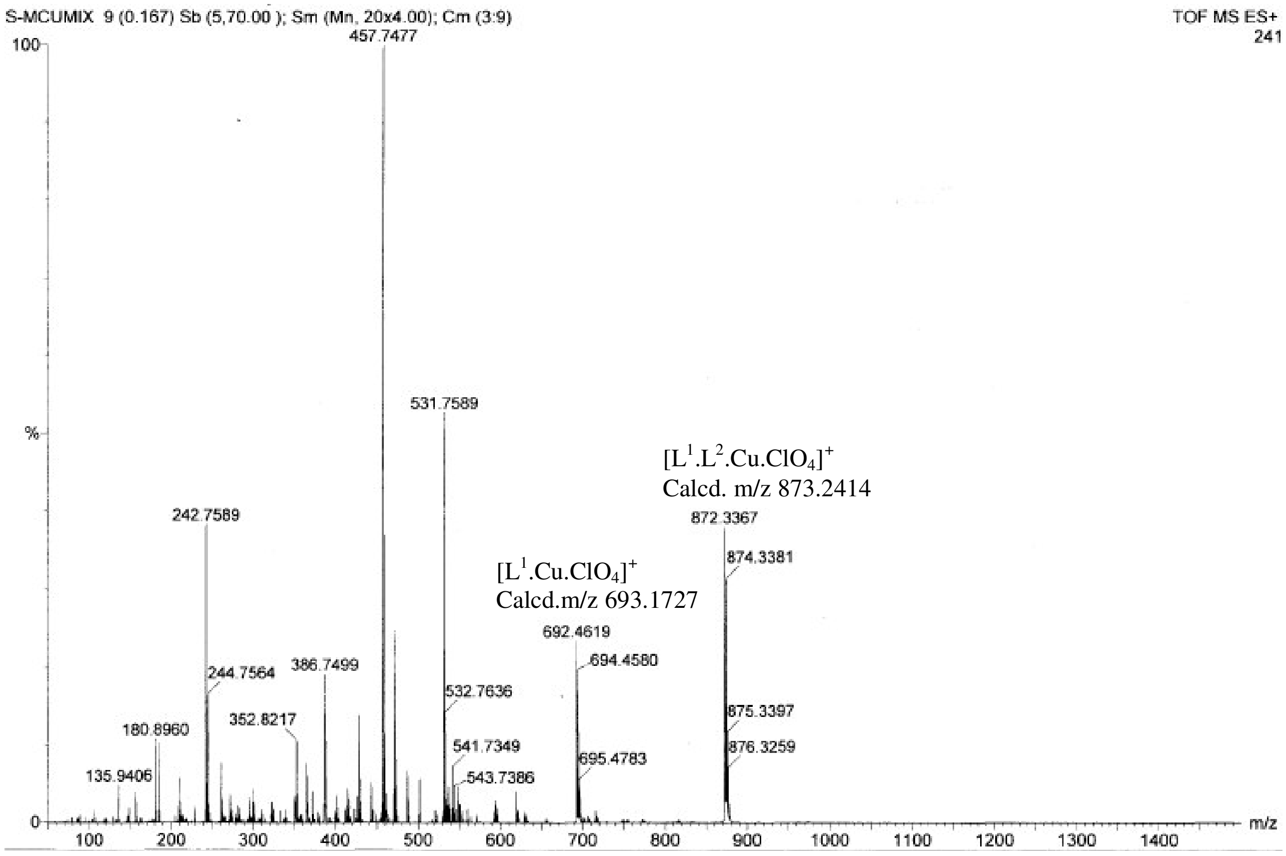


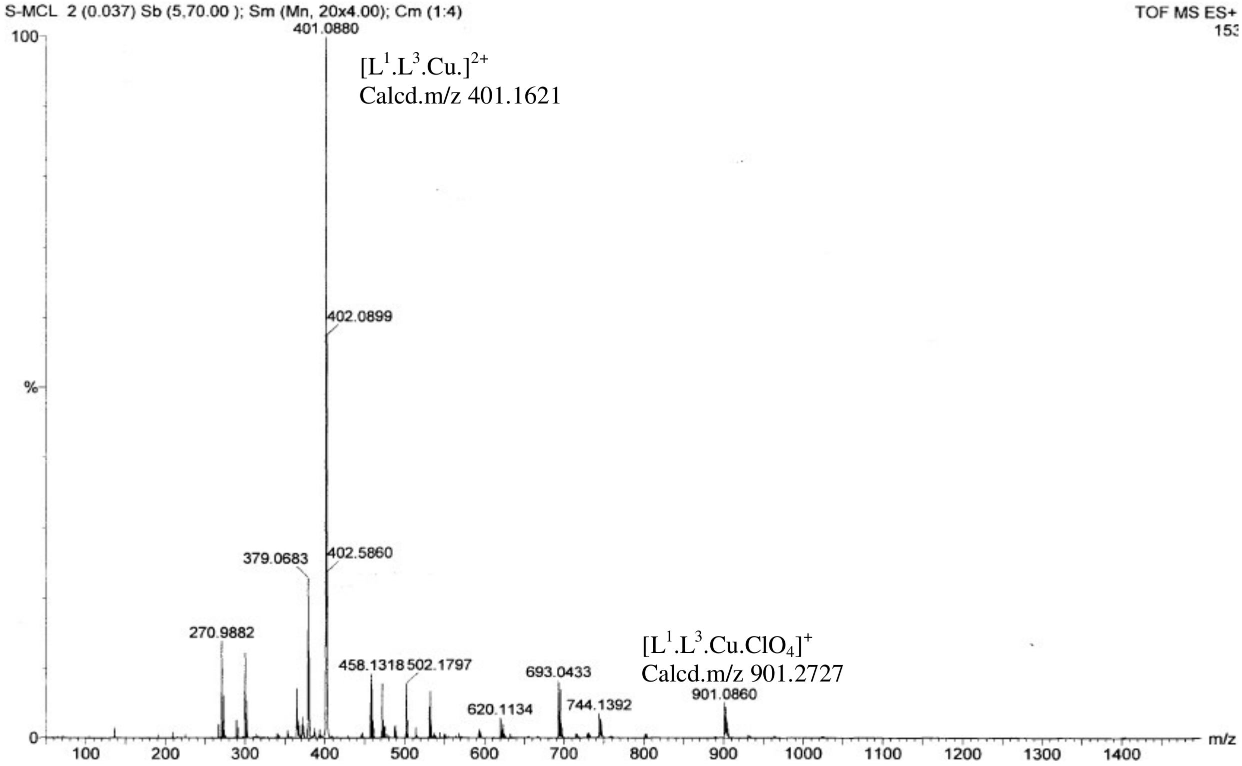
Figure 12S. ESI-MS of complex **2**



$[L^1.L^2.Cu.ClO_4]^+$
Calcd. m/z 873.2414

$[L^1.Cu.ClO_4]^+$
Calcd.m/z 693.1727

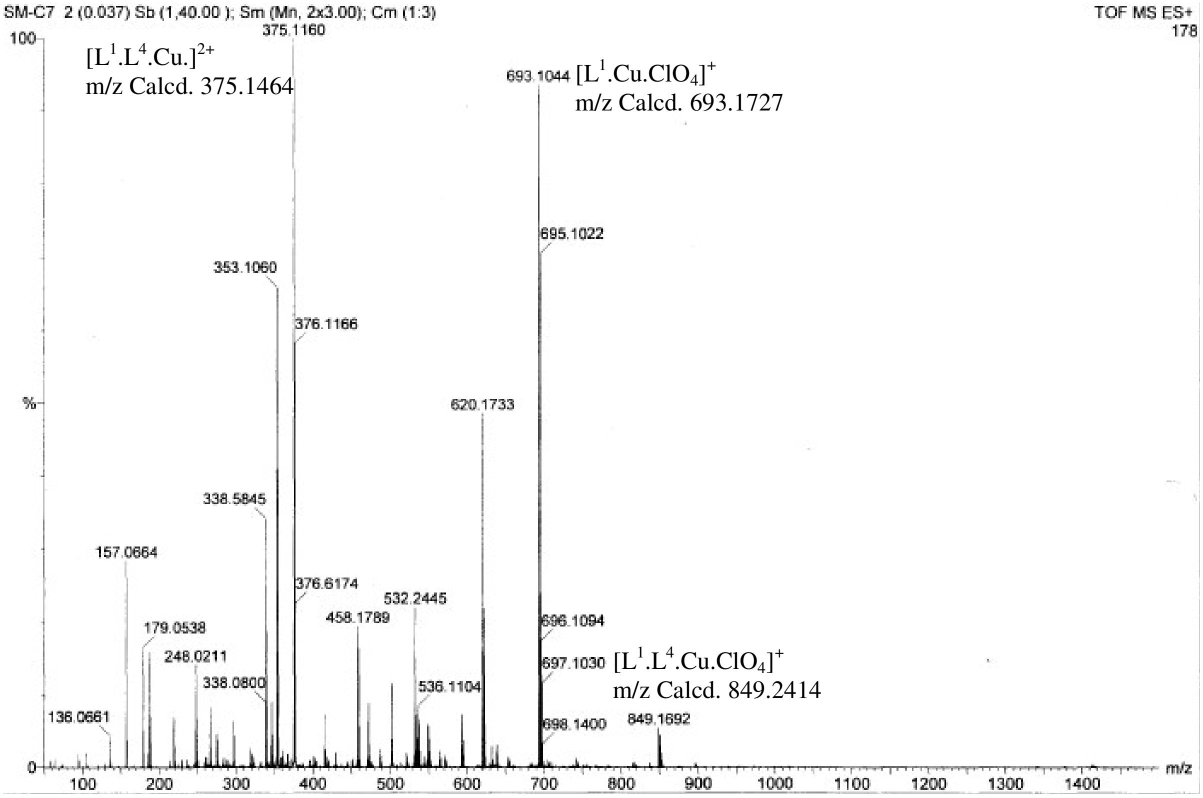
Figur13S. ESI-MS of complex **3**



$[L^1.L^3.Cu.]^{2+}$
Calcd.m/z 401.1621

$[L^1.L^3.Cu.ClO_4]^+$
Calcd.m/z 901.2727

Figure 14S. ESI-MS of complex **4**



$[L^1.L^4.Cu.]^{2+}$
m/z Calcd. 375.1464

$[L^1.Cu.ClO_4]^+$
m/z Calcd. 693.1727

$[L^1.L^4.Cu.ClO_4]^+$
m/z Calcd. 849.2414

Figure 15S. ESI-MS of complex **5**

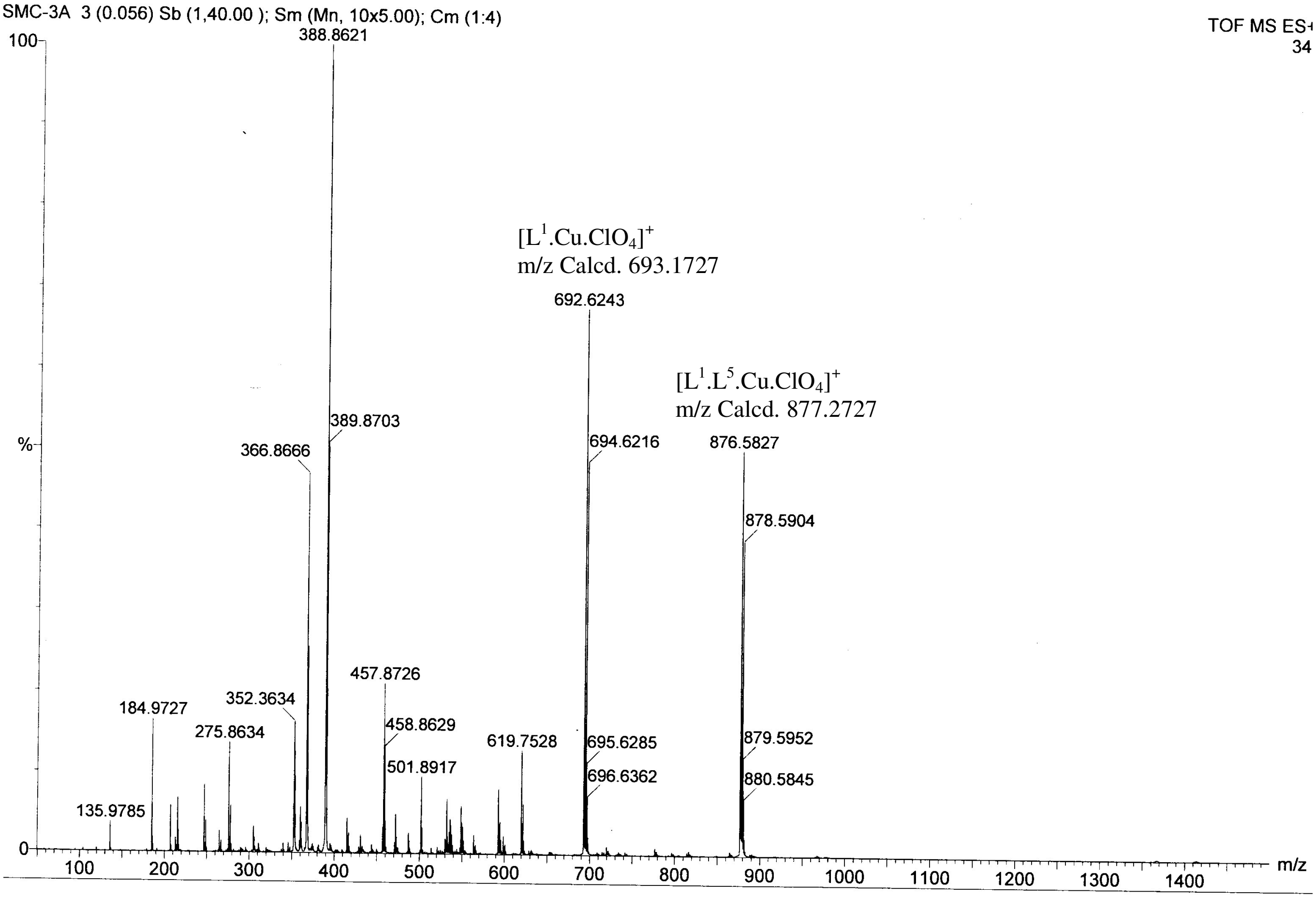


Figure 16S. UV/Vis spectra of $\mathbf{L^1}$ (4 x 10^{-3} M) and Cu^{2+} (4 x 10^{-3} M) upon addition of $\mathbf{L^2}$-$\mathbf{L^5}$ (4 x 10^{-3} M) in methanol

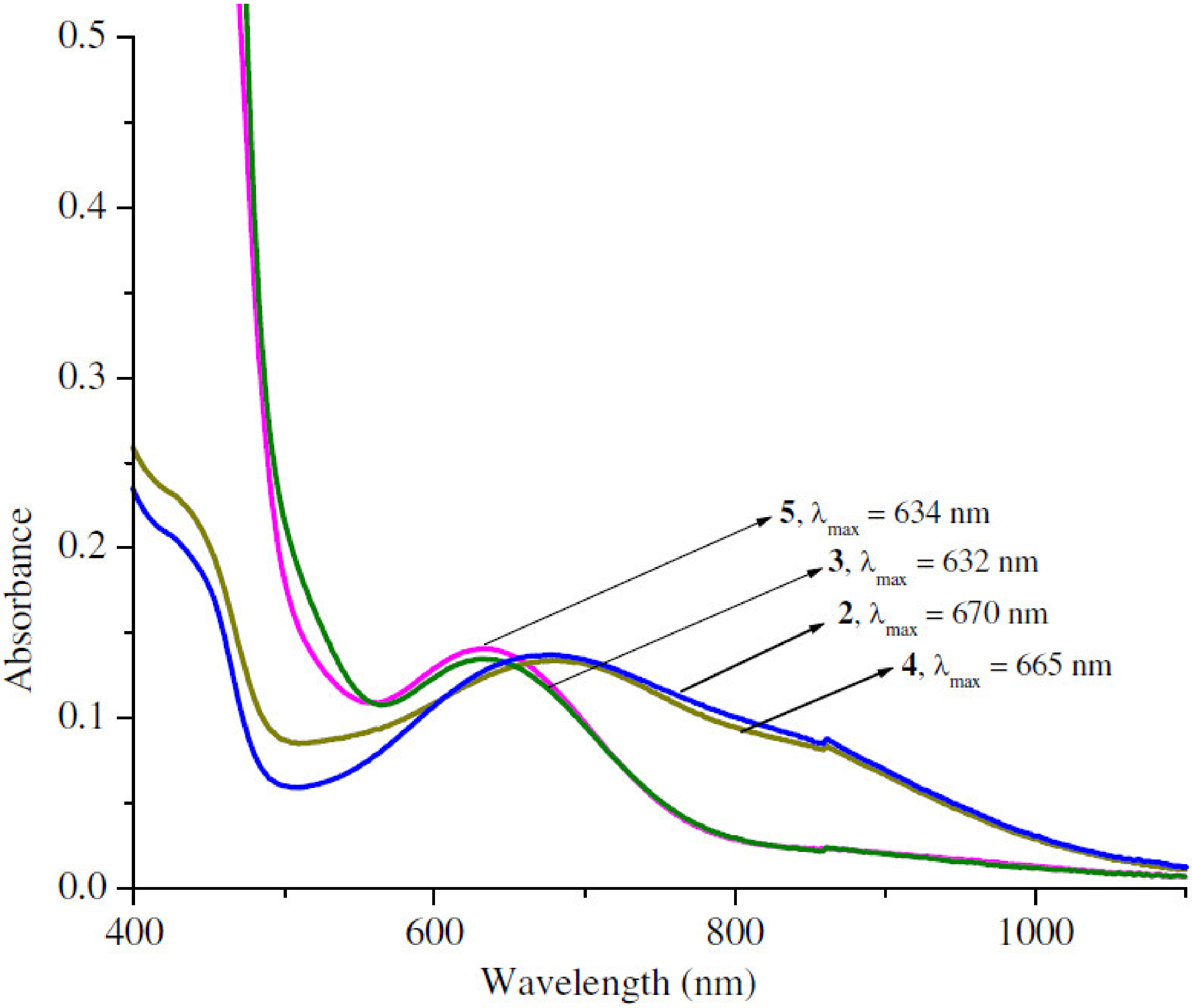


Figure 17S. ESI-MS of the solid that obtained from the equimolar mixtures of **L^1-L^5** and all metal salts in MeOH/CH_2Cl_2 binary solvent system.

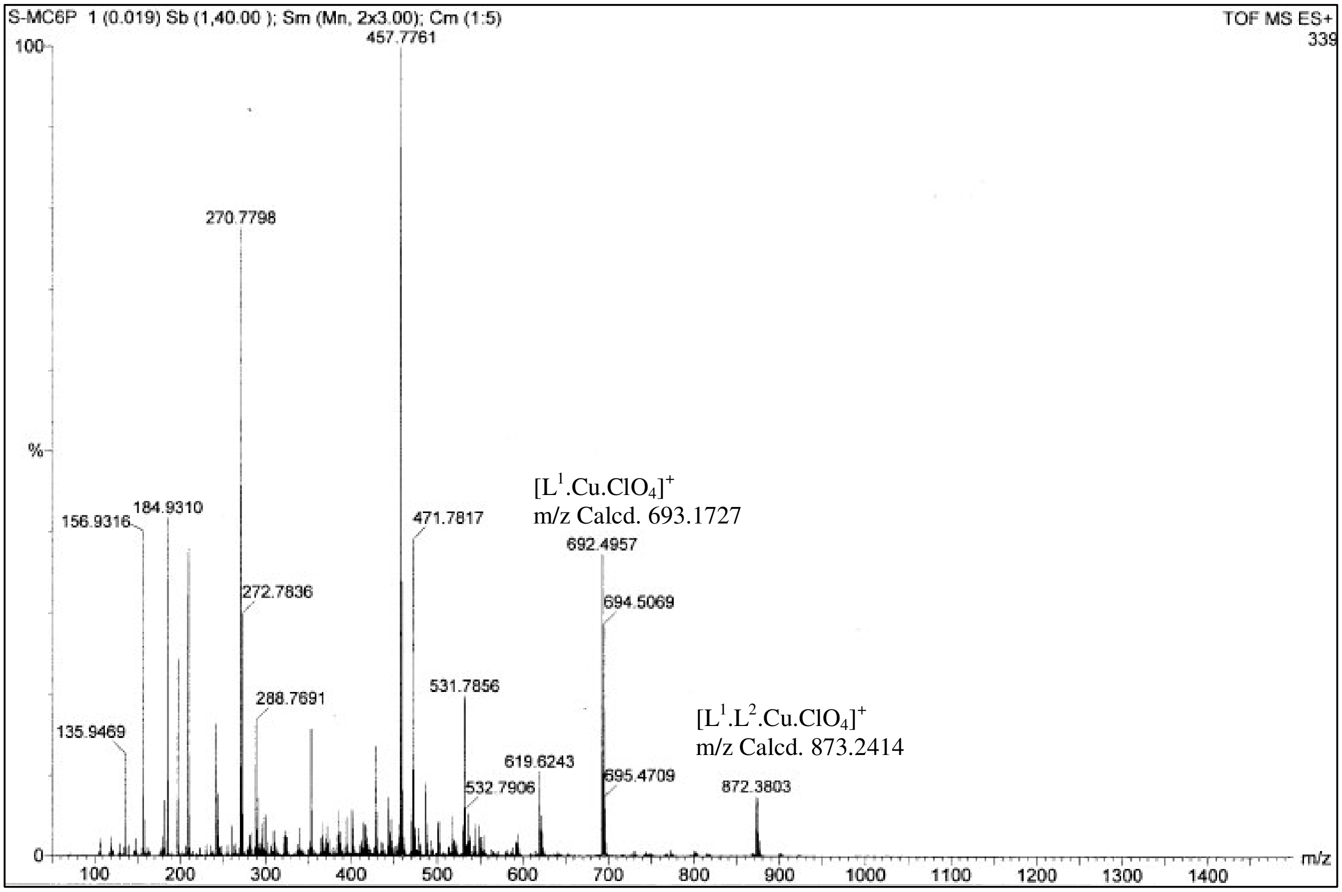


Figure 18S. ESI-MS of a 1:1:1 mixture of solution containing $\mathbf{L^1}$ (4 x 10^{-3} M) and Cu^{2+} (4 x 10^{-3} M) upon addition of a solution mixture of $\mathbf{L^2}$-$\mathbf{L^5}$ (4 x 10^{-3} M, each) in methanol

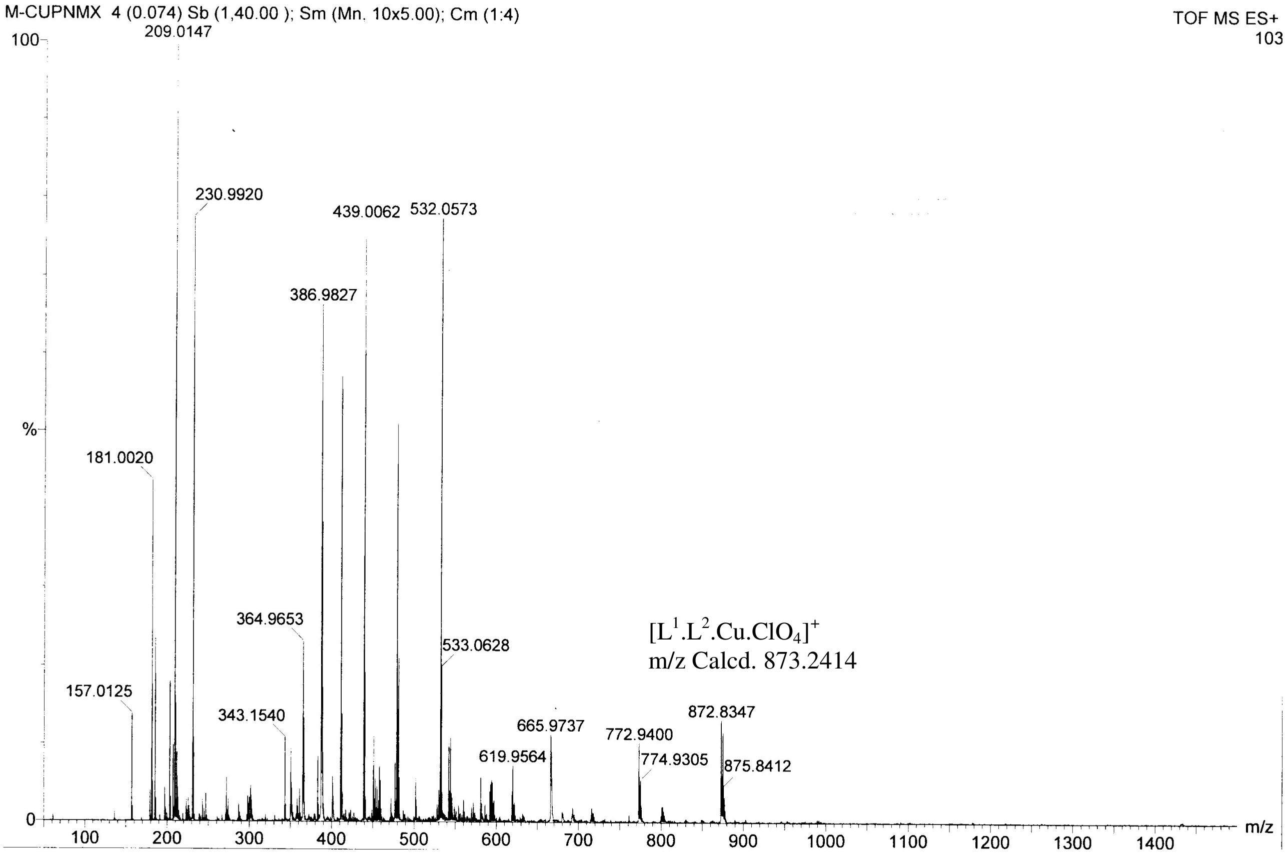


Figure 19S. ESI-MS of a 1:1:1 mixture of solution containing $\mathbf{L^1}$ (4 x 10^{-3} M) and solution mixture of Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}(4 x 10^{-3} M, each) upon addition of a solution $\mathbf{L^2}$ (4 x 10^{-3} M) in methanol

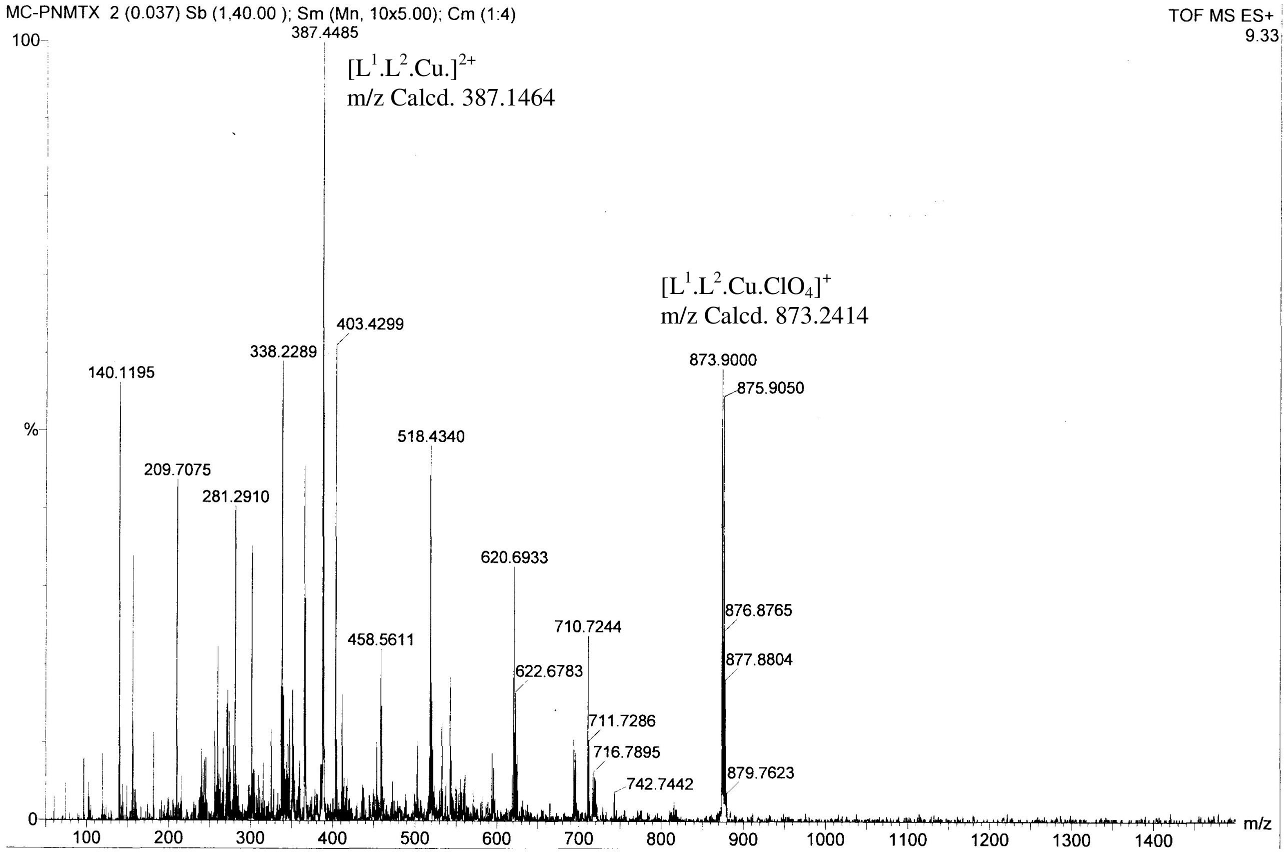
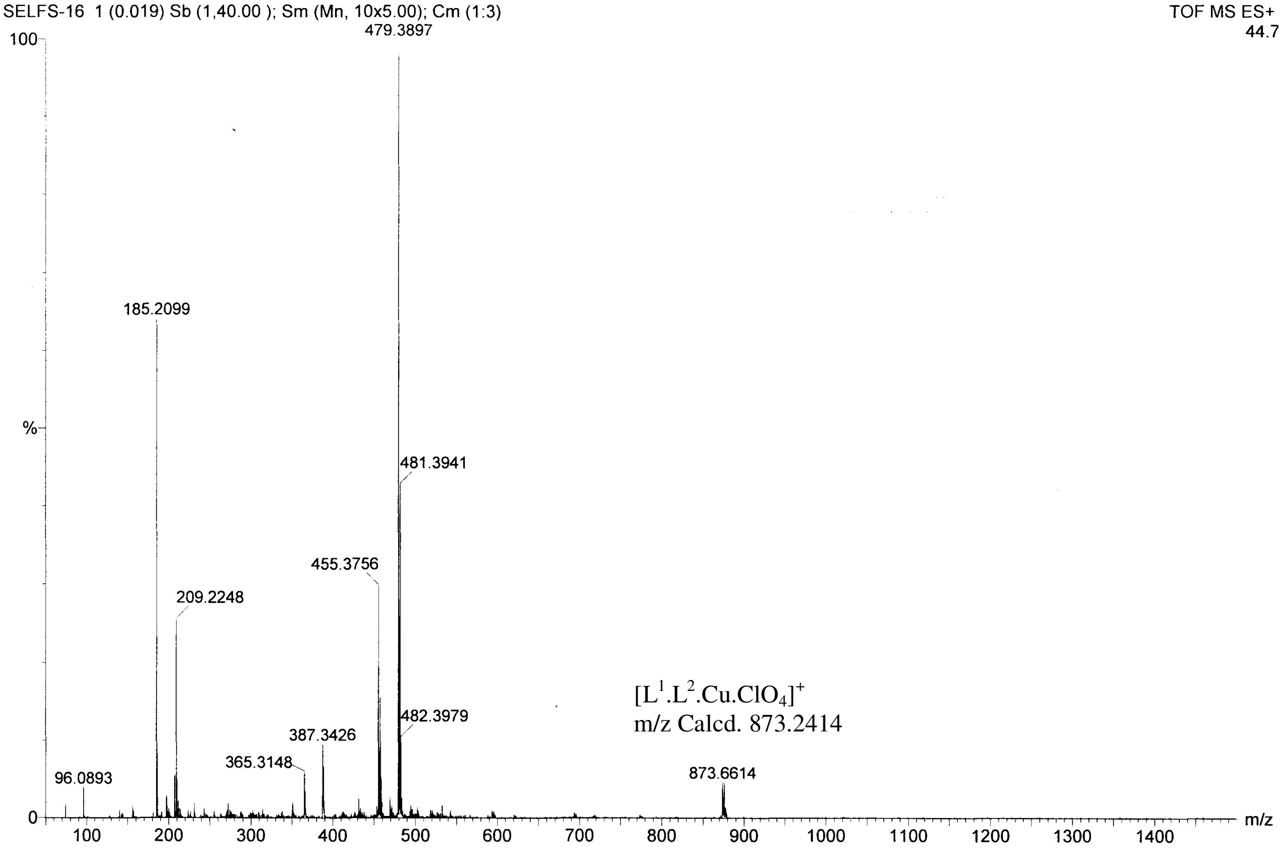


Figure 20S. ESI-MS of a 1:1:1 mixture of solution containing **L^1** (4 x 10^{-3} M) and solution mixture of Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}(4 x 10^{-3} M, each) upon addition of a solution mixture of **L^2-L^5** (4 x 10^{-3} M, each) in methanol



$[L^1.L^2.Cu.ClO_4]^+$
m/z Calcd. 873.2414

Figure 21S. ESI-MS experiment of the mixtures of a sample containing Cu^{2+}, L^1, L^2, L^3, L^4 and L^5 in a 4:4:1:1:1:1 ratio in methanol. 50 μL solution of Cu^{2+} (4x10^{-3}M), L^1 (4x10^{-3}M), L^2 (1x10^{-3}M), L^3 (1x10^{-3}M), L^4 (1x10^{-3}M) and L^5 (1x10^{-3}M) were mixed.

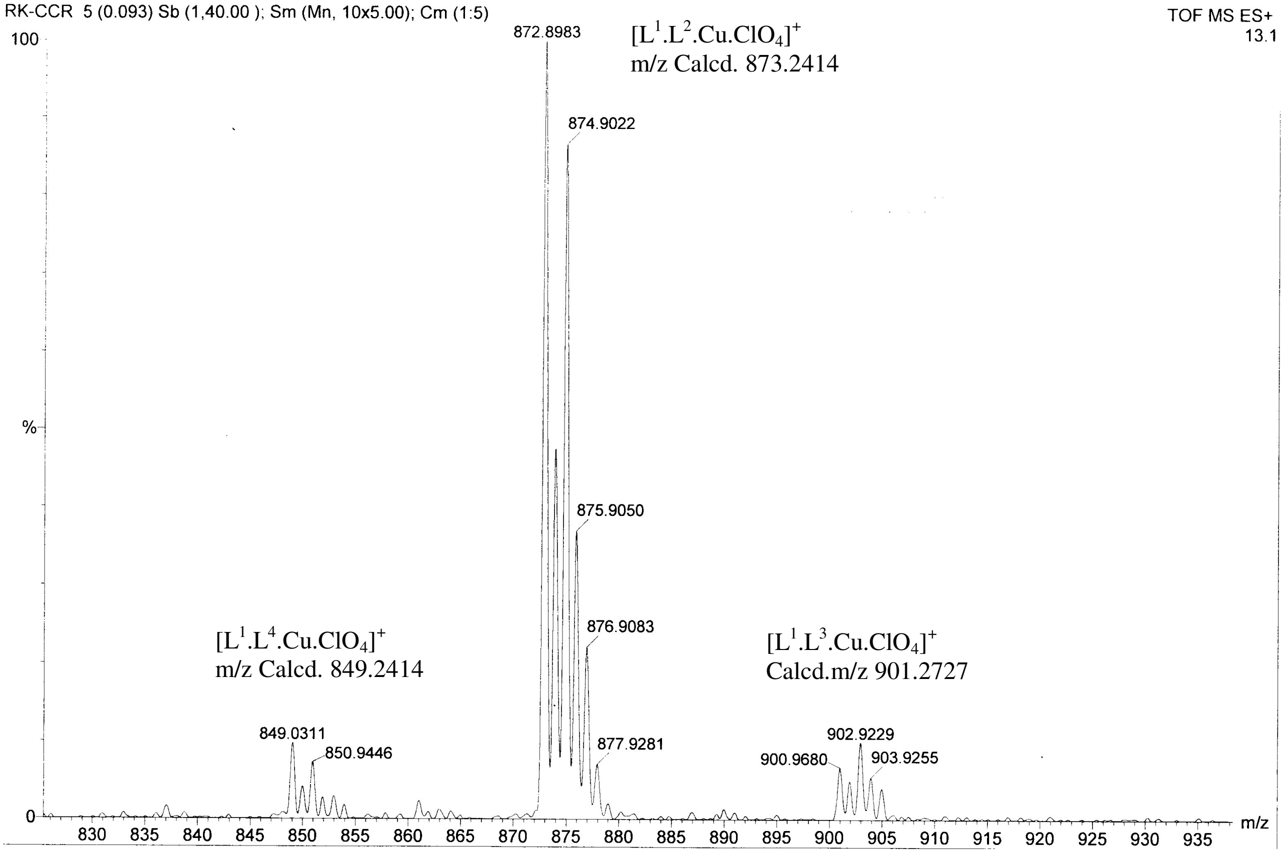


Table 1S. Crystallographic table of complex **1**.

	1
Emprical formula	C_{34} H_{42} Cl_2 Cu N_7 O_{13}
Formula weight	891.17
Crystal system	Monoclinic
Space group	P21/c
a (Å)	9.328(2)
b (Å)	29.816(6)
c (Å)	15.503(3)
α (deg)	90.00
β (deg)	109.638(10)
γ (deg)	90.00
V (Å^3)	4061.0(14)
Z	4
d_{calcd} (g/cm^3)	1.454
Crystal size (mm^3)	0.12 x 0.08 x 0.06
F(000)	1840
μ Mo Kα (mm^{-1})	0.740
T (K)	100 (2)
θ range (deg)	1.37 -18.22
Reflections collected	14451
Independent reflections	2890
R(int)	0.1059
Refined parameters	516
R1;wR2	0.0609 ; 0.1123
GOF (F^2)	1.028
Residual electron density	0.340 , -0.310

Table 2S. Crystallographic table of complex **2**

	2
Emprical formula	C_{42} H_{45} Cl_2 Cu N_7 O_{14}
Formula weight	991.17
Crystal system	Monoclinic
Space group	P21/c
a (Å)	11.7929(9)
b (Å)	11.6986(9)
c (Å)	32.650(2)
α (deg)	90.00
β (deg)	97.443(2)
γ (deg)	90.00
V (Å^3)	4466.4(6)
Z	4
d_{calcd} (g/cm^3)	1.474
Crystal size (mm^3)	0.29 x 0.12 x 0.09
F(000)	2024
μ Mo Kα (mm^{-1})	0.129
T (K)	100 (2)
θ range (deg)	1.3-24.3
Reflections collected	38647
Independent reflections	7219
R(int)	0.0363
Refined parameters	589
R1;wR2	0.0591 ; 0.1660
GOF (F^2)	1.060
Residual electron density	0.610 , -0.491

Figure 22S.EPR spectrum of complex **1** in acetonitrile solution

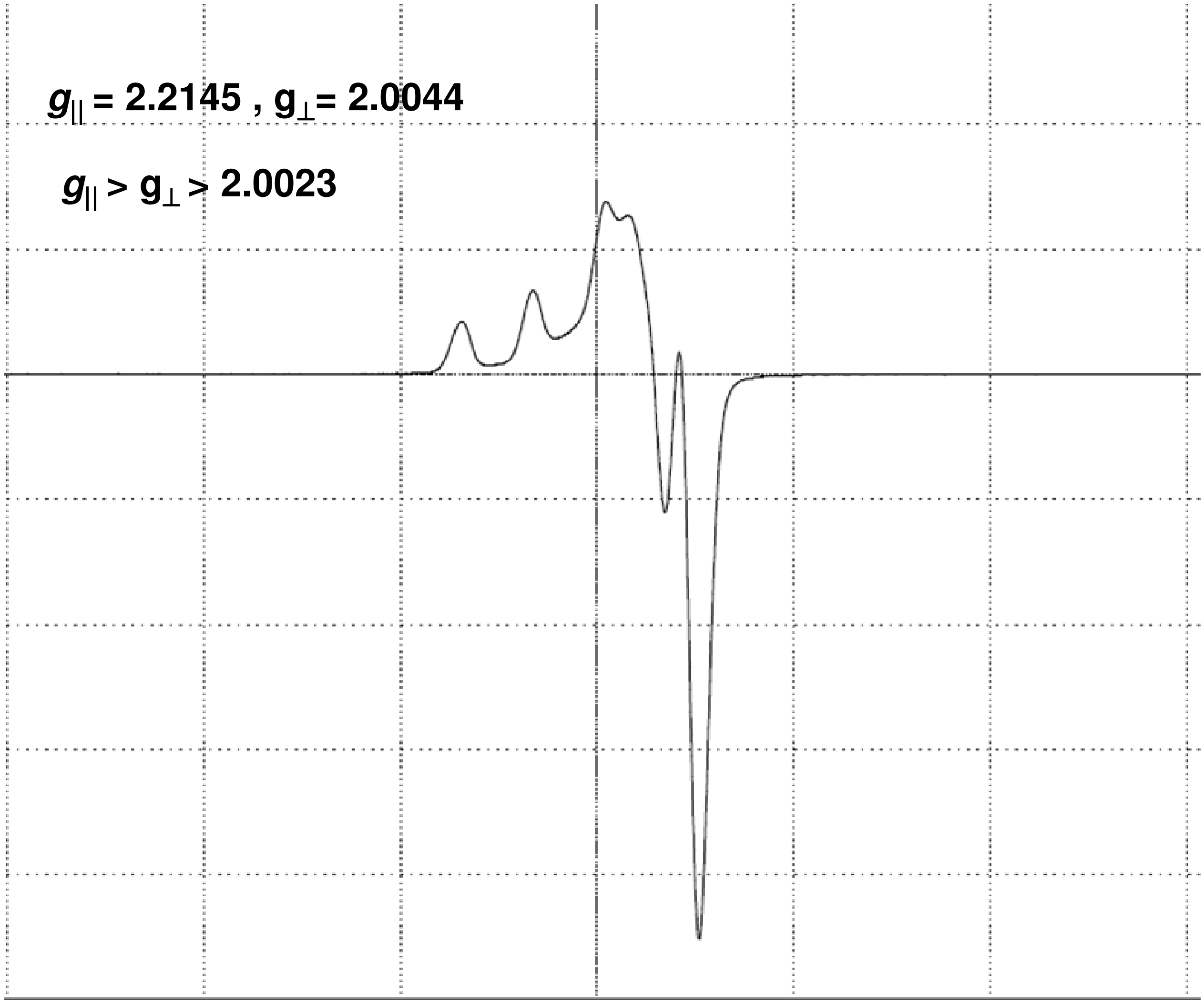


Figure 23S. EPR spectrum of complex **2** in acetonitrile solution

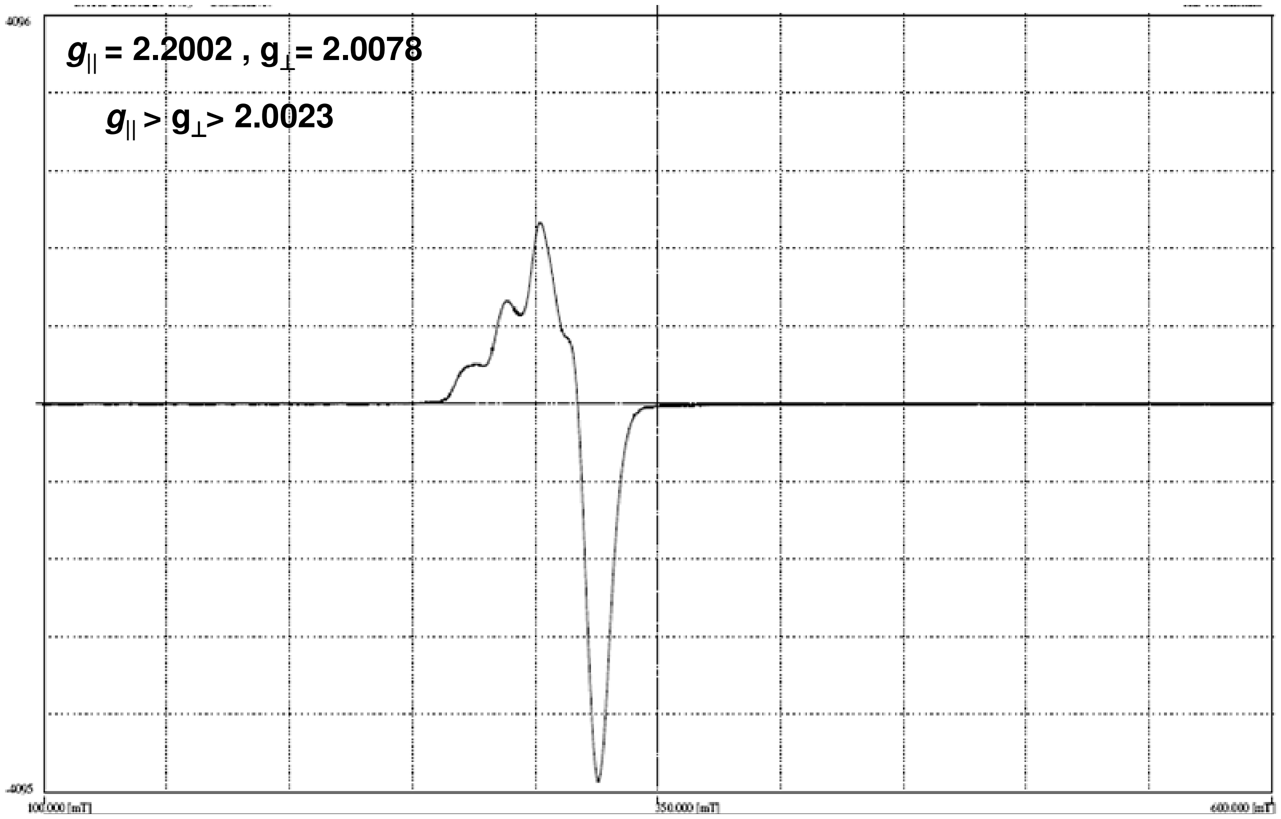
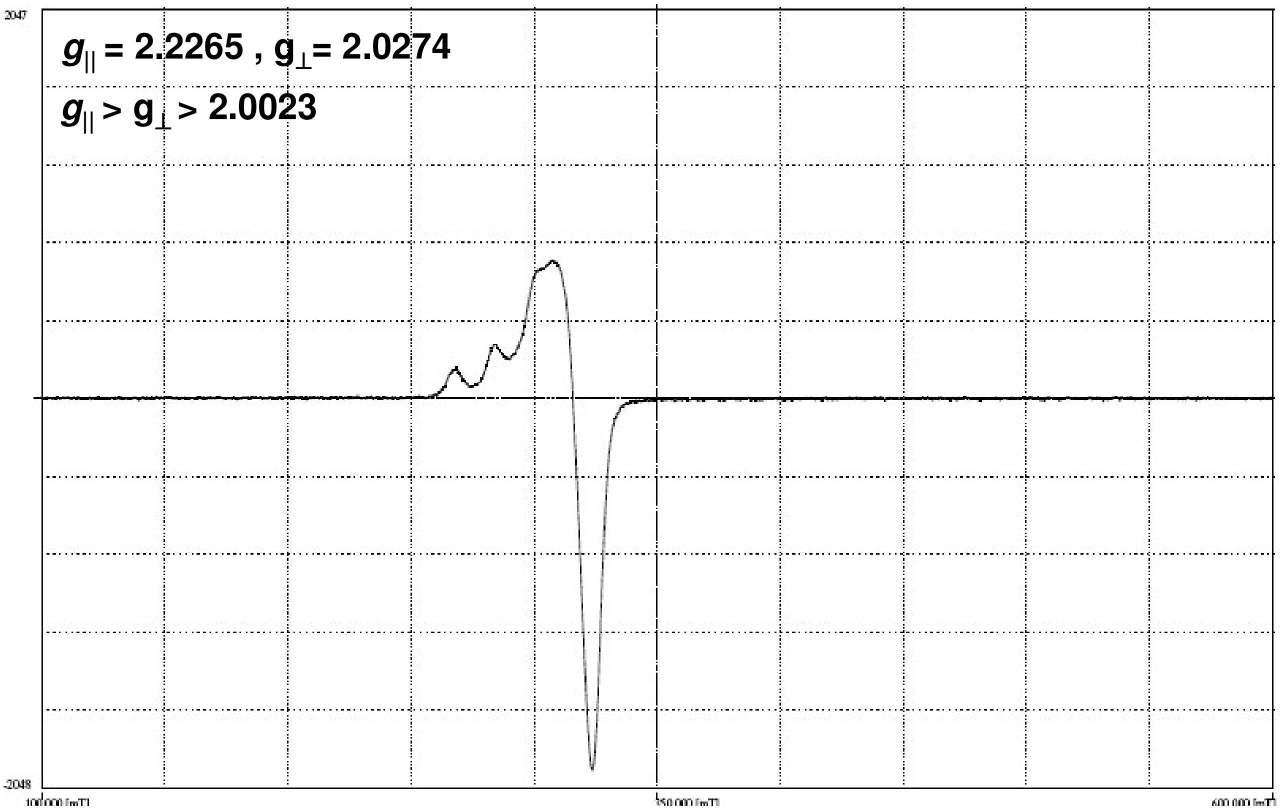


Figure 24S. EPR spectrum of complex **3** in acetonitrile solution


$g_{||} = 2.2265$, $g_{\perp} = 2.0274$

$g_{||} > g_{\perp} > 2.0023$

Figure 25S. EPR spectrum of complex **4** in acetonitrile solution

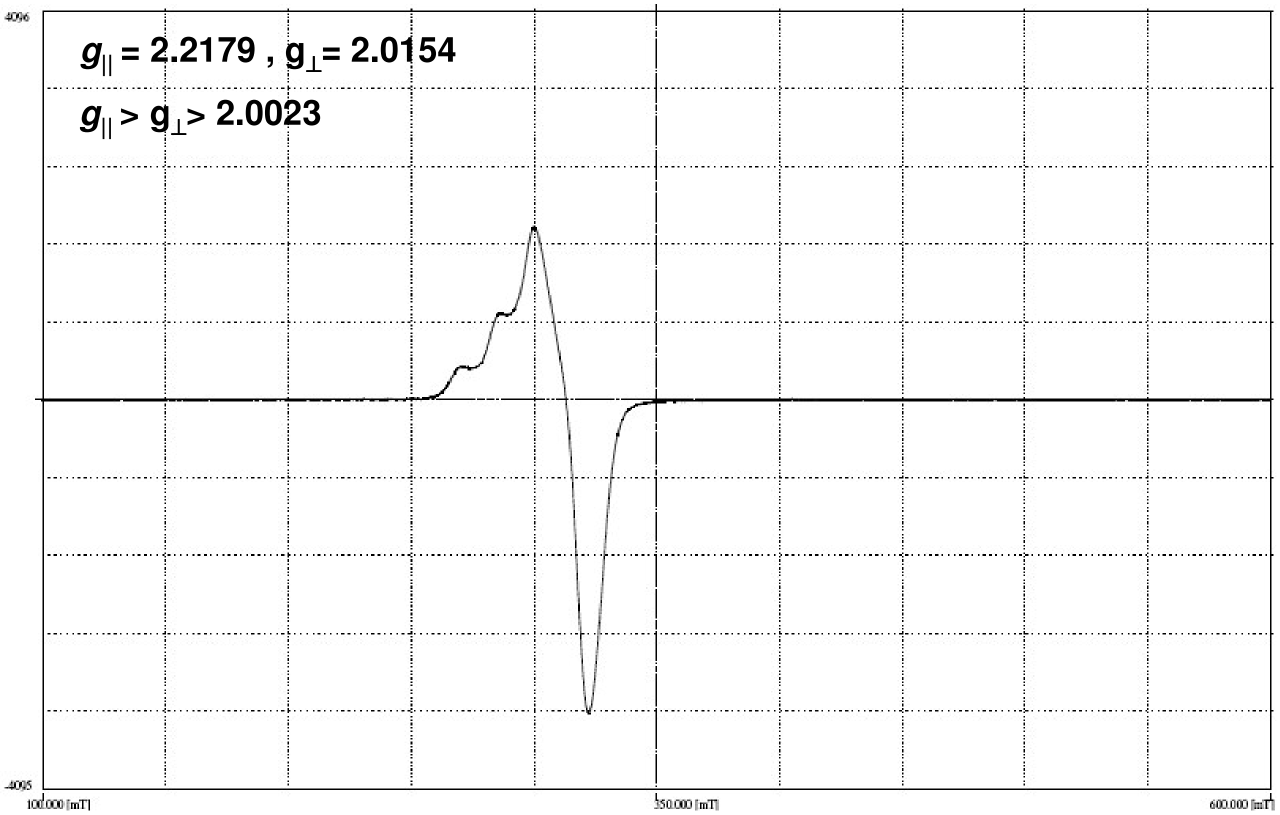


Figure 26S. EPR spectrum of complex **5** in acetonitrile solution

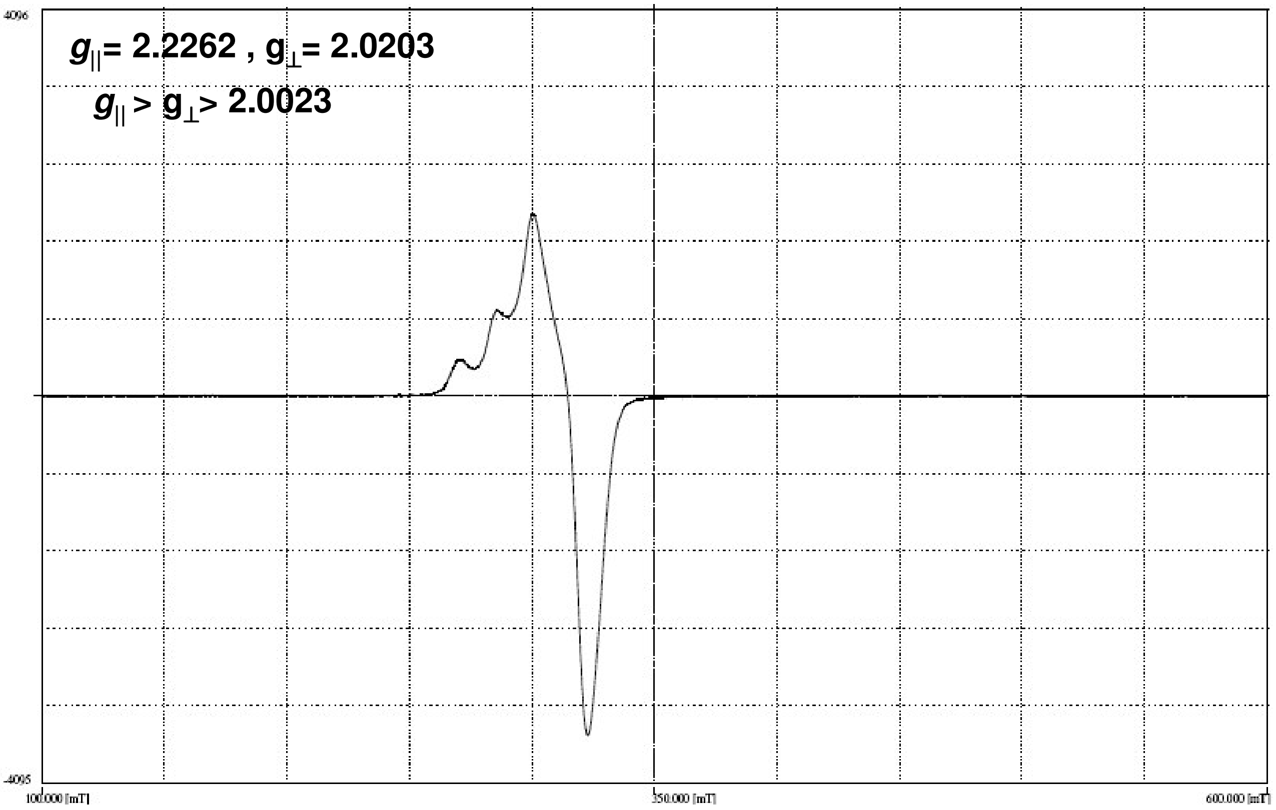
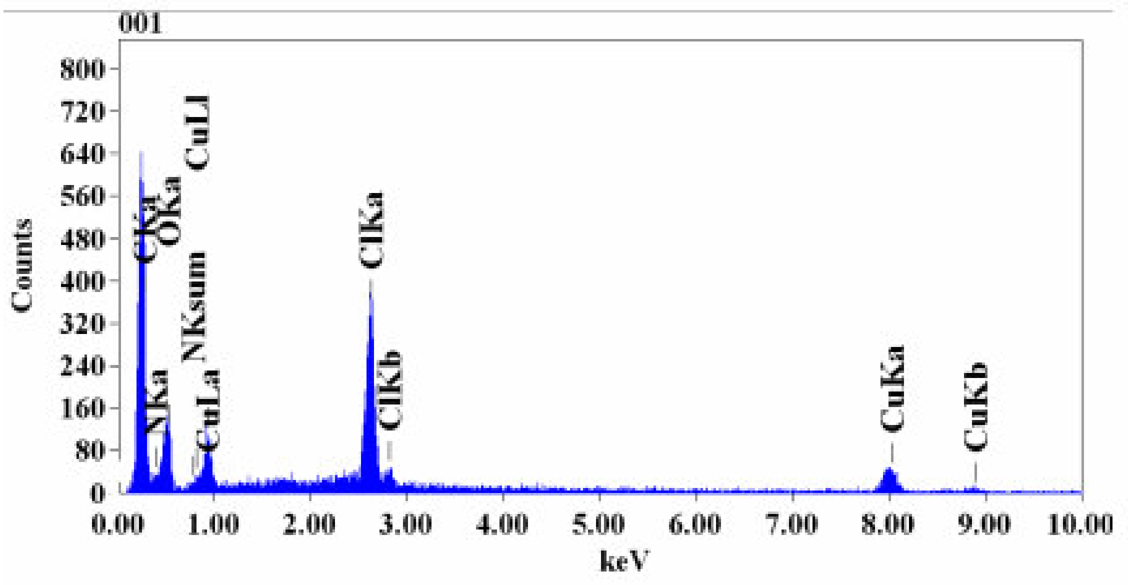


Figure 27S. Energy dispersion X-ray (EDX) spectrum of solid obtained from path B



Scheme 2S. Possible ternary complexes in cases of paths A (first row) and B (second row)

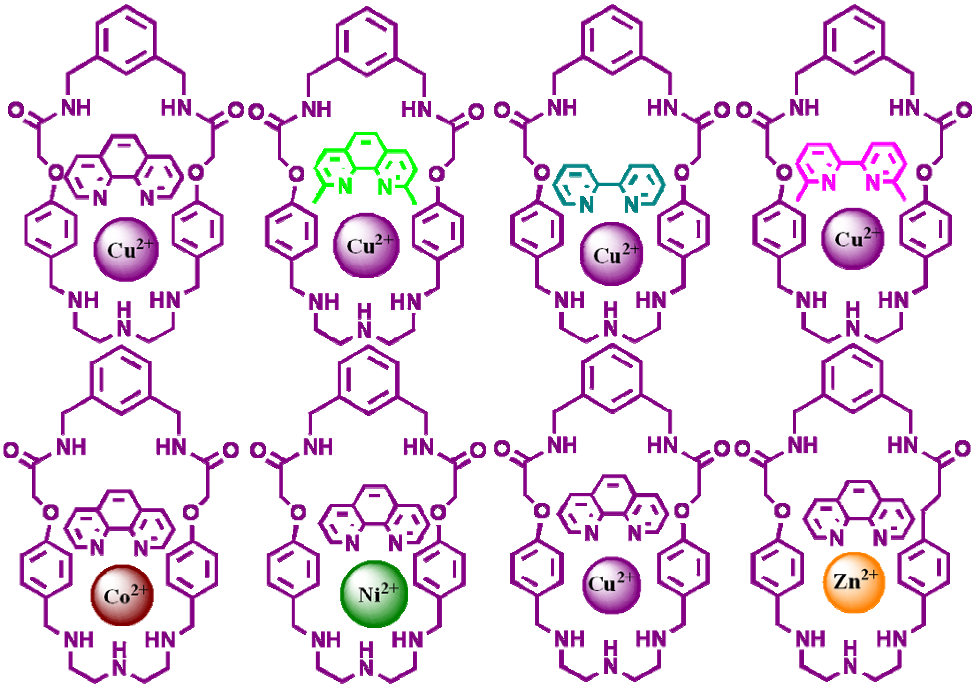


Figure 28S. UV-Vis titration profile of $\mathbf{L^1}$+ $\mathbf{L^2}$ (5 x 10^{-3}M, each) with Cu^{2+}(1 x 10^{-2} M) in methanol, Selected UV-Vis spectra are shown for clarity whereas sigmoidal fits show more numbers of points.

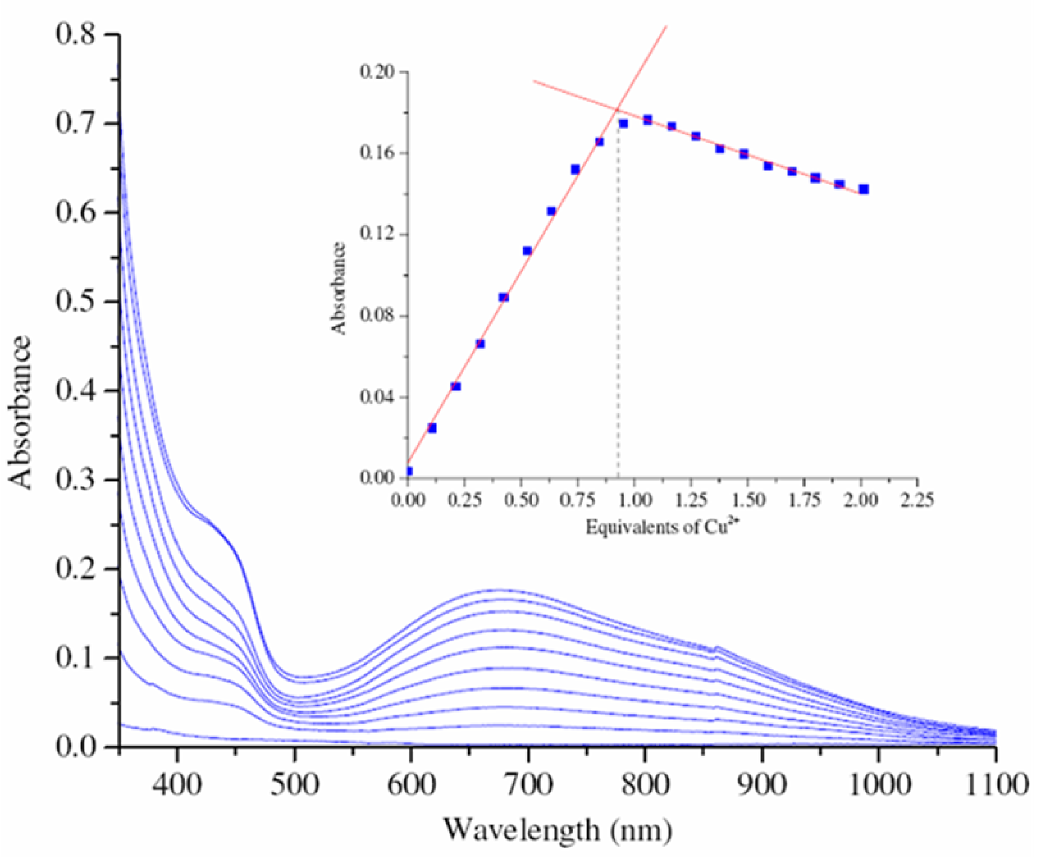


Table 3S: Selected bond length (Å) and bond angles (°) of complex **1**.

Cu1-N1	2.008 (9) Å
Cu1-N2	2.043 (10) Å
Cu1-N5	2.044 (10) Å
Cu1-N6	2.232 (12) Å
Cu1-N7	1.980 (12) Å

<N1···Cu1···N2	85.4 (4)°
<N2···Cu1···N7	92.1 (4)°
<N7···Cu1···N5	90.7 (4)°
<N5···Cu1···N1	84.2 (4)°
<N1···Cu1···N6	96.4 (4)°
<N2···Cu1···N6	95.4 (4)°
<N7···Cu1···N6	113.4 (4)°
<N5···Cu1···N6	98.0 (4)°
<N1···Cu1···N7	150.2 (4)°
<N2···Cu1···N5	163.8 (4)°

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1) SAINT and *XPREP*, 5.1 ed.; Siemens Industrial Automation Inc.: Madison, WI, 1995. G. M. Sheldrick.
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6) Mercury 2.2 Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 2003-2004.