Synthesis, characterization of the amido-conjugates of 1, 1'-methylene-bis(2-naphthol) and the recognition of Cu^{2+} in aqueous acetonitrile

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Electronic Supplementary Information

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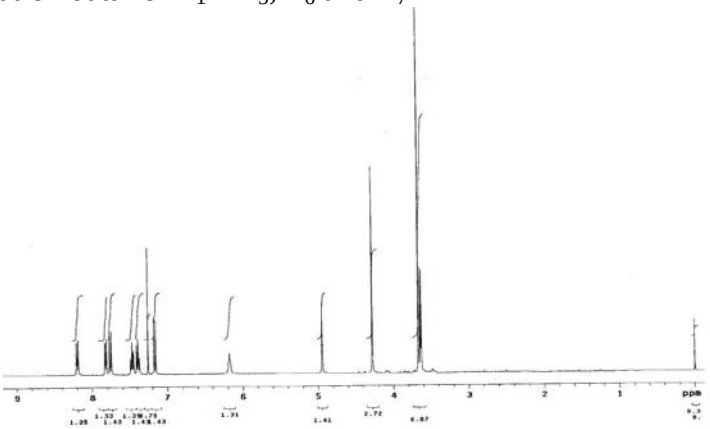
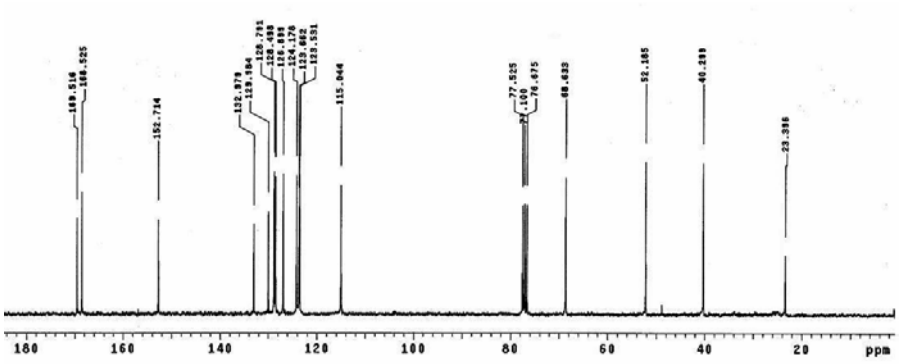
S01. Characterization data for L_1 – L_5, L_6 and L_7

(a)



(b)



(c)

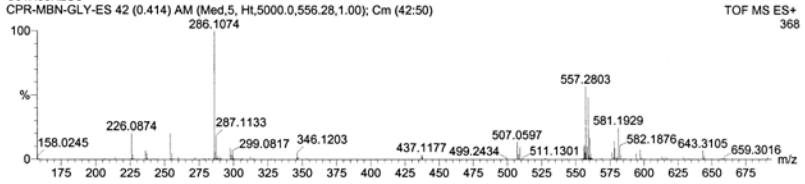
Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
169 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Micromass : Q-Tof micro (YA-105) Dept. Of Chemistry I.I.T.(B) 14-Jun-201114:44:40

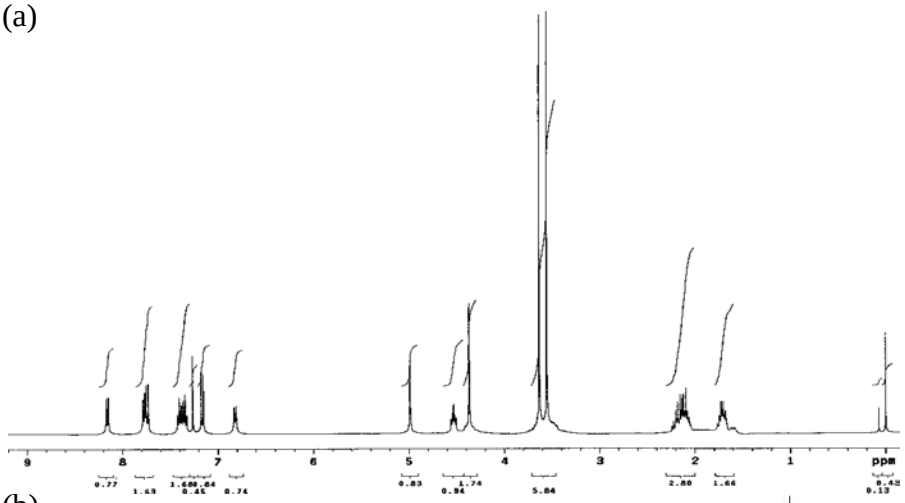
C31H30N2O8
CPR-MBN-GLY-ES 42 (0.414) AM (Med,5, Ht,5000.0,556.28,1.00); Cm (42:50) TOF MS ES+
368



Minimum:				-1.5		
Maximum:		200.0	20.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
559.2089	559.2080	0.9	1.6	17.5	1	C31 H31 N2 O8

Figure S01(a). Characterization of **L_1** (a) ^{1}H NMR, (b) ^{13}C NMR and (c) HRMS

(a)



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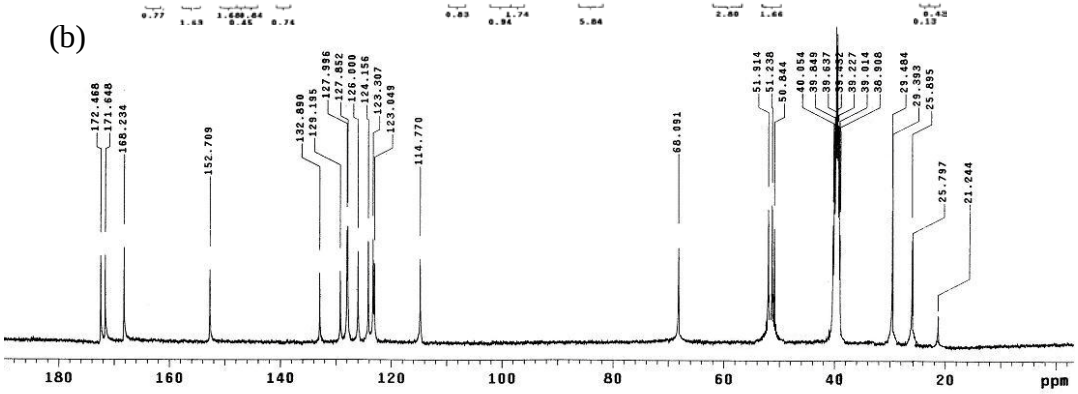


(c)

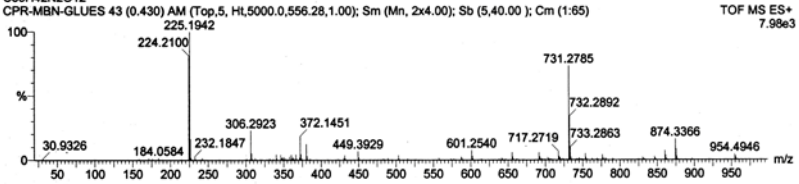
Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
35725 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Micromass : Q-Tof micro (YA-105) Dept. Of Chemistry I.I.T.(B) 22-Jun-201114:12:07

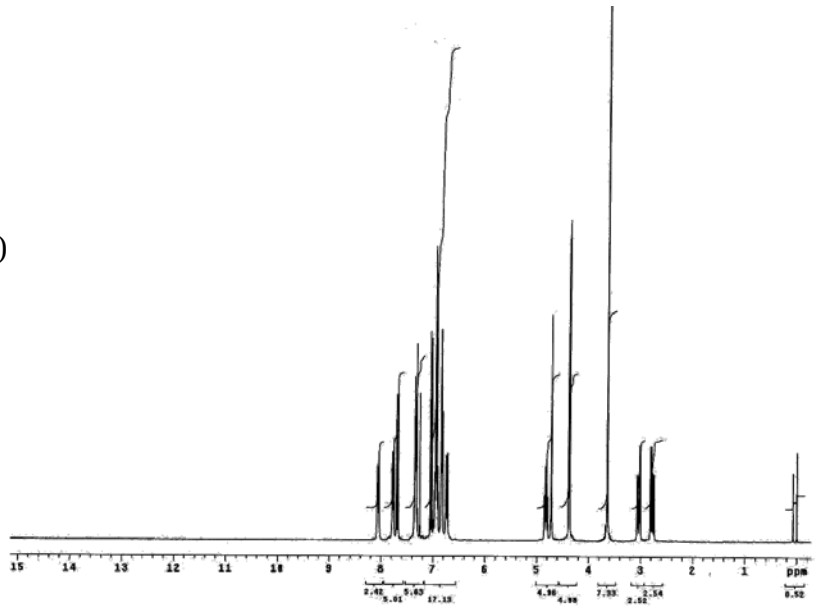
C39H42N2O12
CPR-MBN-GLUES 43 (0.430) AM (Top,5, Ht,5000.0,556.28,1.00); Sm (Mn, 2x4.00); Sb (5,40.00); Cm (1:65) TOF MS ES+ 7.98e3



Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
731.2785	731.2816	-3.1	-4.2	19.5	1	C39 H43 N2 O12

Figure S01(b). Characterization of $\mathbf{L}_2$**:** (a) ^{1}H NMR, (b) ^{13}C NMR and (c) HRMS

(a)



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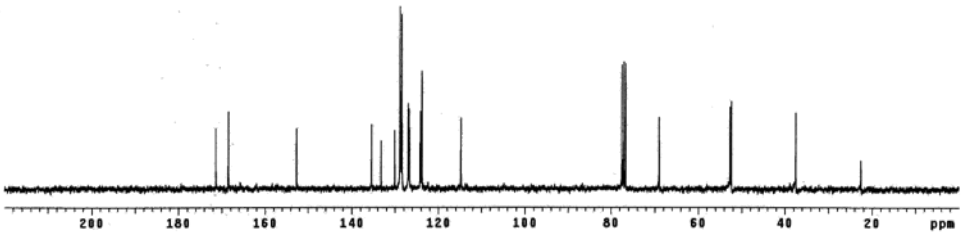


(c)

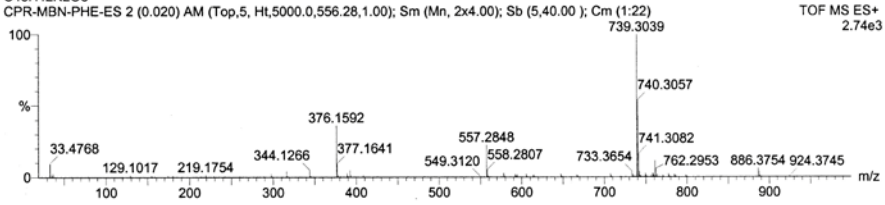
Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Micromass : Q-Tof micro (YA-105) Dept. Of Chemistry I.I.T.(B) 14-Jun-201115:10:20

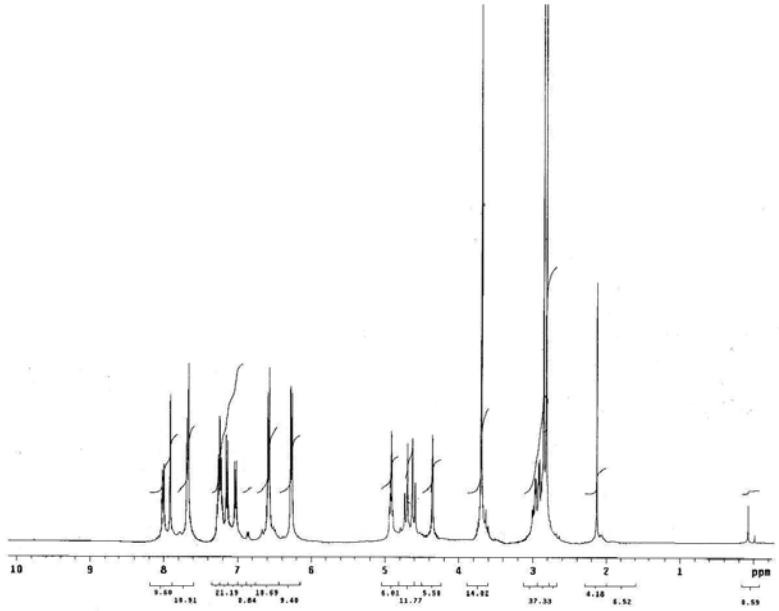
C45H42N2O8
CPR-MBN-PHE-ES 2 (0.020) AM (Top,5, Ht,5000.0,556.28,1.00); Sm (Mn, 2x4.00); Sb (5,40.00); Cm (1:22) TOF MS ES+ 2.74e3



Minimum:				-1.5		
Maximum:		200.0	20.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
739.3039	739.3019	2.0	2.6	25.5	1	C45 H43 N2 O8

Figure S01(c). Characterization of **L_3:** (a) ^{1}H NMR, (b) ^{13}C NMR and (c) HRMS

(a)



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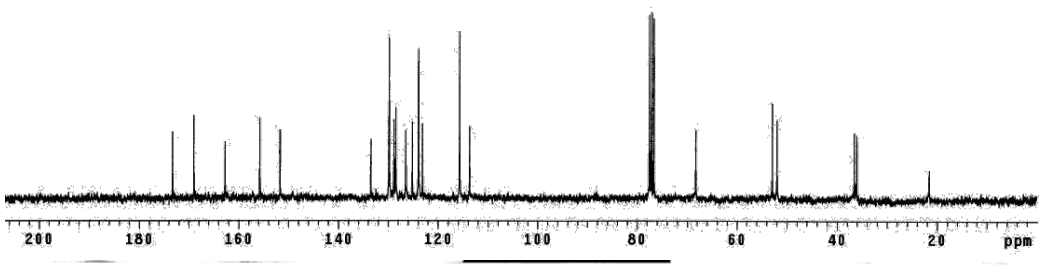


(c)

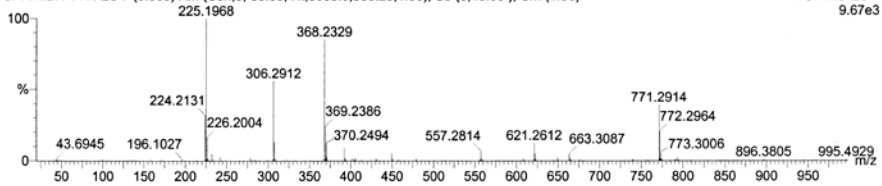
Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
25 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Micromass : Q-Tof micro (YA-105) Dept. Of Chemistry I.I.T.(B) 14-Jun-201115:22:05

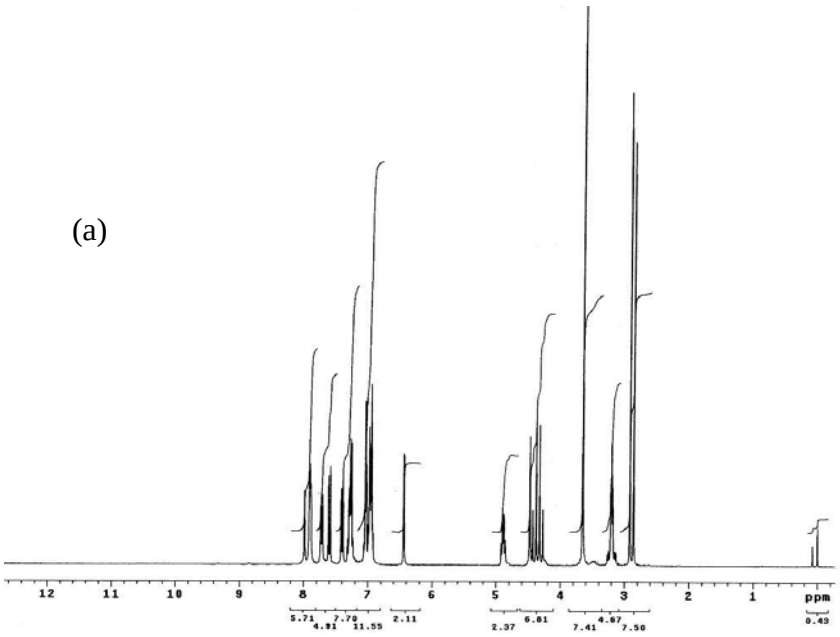
C45H42N2O10
CPR-MBN-TYR-ES 7 (0.069) AM (Cen,5, 80.00, Ht,5000.0,556.28,1.00); Sb (5,40.00); Cm (1:36) TOF MS ES+
9.67e3



Minimum:				-1.5		
Maximum:		200.0	20.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
771.2914	771.2918	-0.4	-0.5	25.5	1	C45 H43 N2 O10

Figure S01(d). Characterization of $\mathbf{L_4}$**:** (a) ^{1}H NMR, (b) ^{13}C NMR and (c) HRMS

(a)



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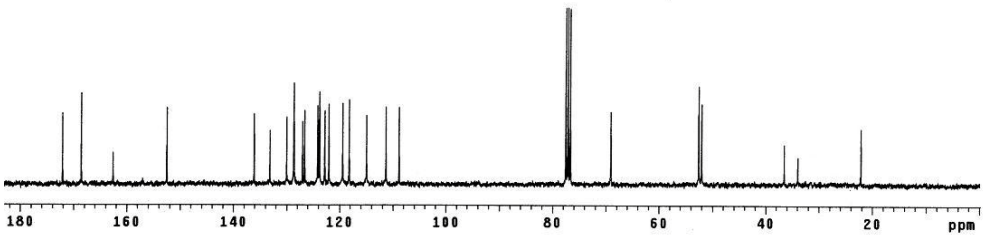


(c)

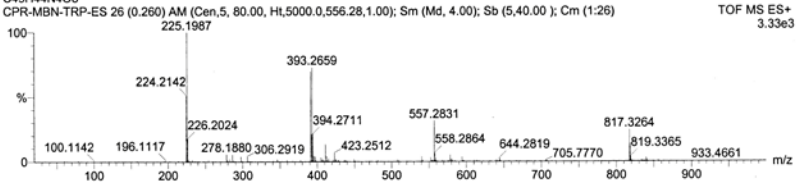
Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
305 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Micromass : Q-Tof micro (YA-105) Dept. Of Chemistry I.I.T.(B) 14-Jun-201114:56:06

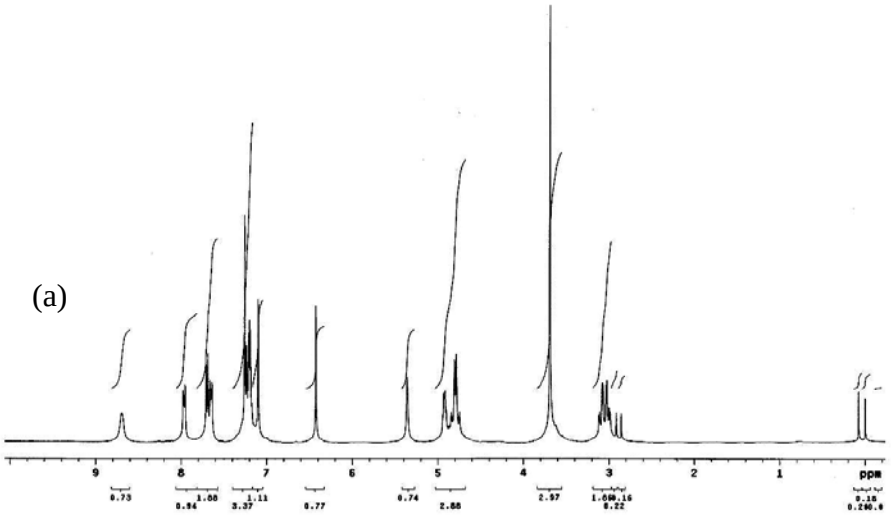
C49H44N4O8
CPR-MBN-TRP-ES 26 (0.260) AM (Cen,5, 80.00, Ht,5000.0,556.28,1.00); Sm (Md, 4.00); Sb (5,40.00); Cm (1:26) TOF MS ES+ 3.33e3



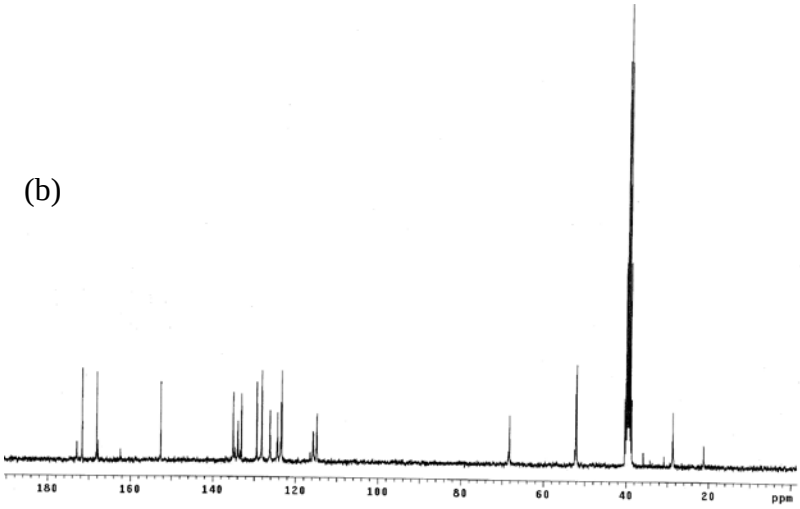
Minimum:				-1.5		
Maximum:		200.0	20.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
817.3264	817.3237	2.7	3.3	29.5	1	C49 H45 N4 O8

Figure S01(e). Characterization of $\mathbf{L_5}$**:** (a) ^{1}H NMR, (b) ^{13}C NMR and (c) HRMS

(a)



(b)



(c)

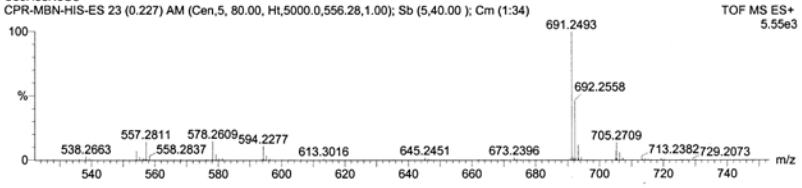
Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
381 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Micromass : Q-Tof micro (YA-105) Dept. Of Chemistry I.I.T.(B) 14-Jun-201114:26:17

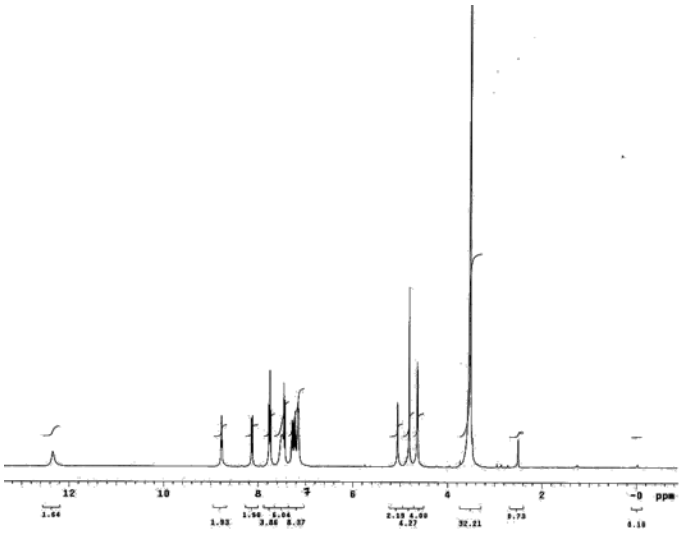
C39H38N6O8
CPR-MBN-HIS-ES 23 (0.227) AM (Cen,5, 80.00, Ht,5000.0,556.28,1.00); Sb (5,40.00); Cm (1:34) TOF MS ES+ 5.55e3



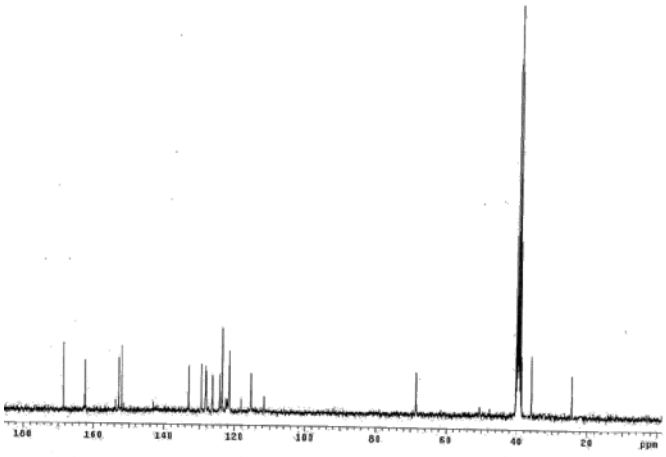
Minimum:				-1.5		
Maximum:		200.0	20.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
719.2842	719.2829	1.3	1.8	23.5	1	C39 H39 N6 O8

Figure S01(f). Characterization of **L_6:** (a) ^{1}H NMR, (b) ^{13}C NMR and (c) HRMS

(a)



(b)



(c)

Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
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Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
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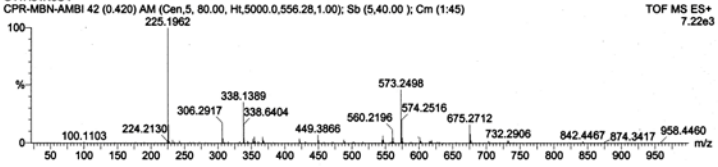
Micromass : Q-Tof micro (YA-105) Dept. Of Chemistry I.I.T.(B) 22-Jun-201114:20:28

C41H34N6O4
CPR-MBN-AMBI 42 (0.420) AM (Cen,5, 80.00, Ht,5000.0,556.28,1.00); Sb (5,40.00); Cm (1:45) TOF MS ES+
7.22e3



Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
675.2712	675.2720	-0.7	-1.1	27.5	1	C41 H35 N6 O4

Figure S01(g). Characterization of **L_7:** (a) ^{1}H NMR, (b) ^{13}C NMR and (c) HRMS

S02. Single crystal XRD structure for ligand $\mathbf{L_2}$.

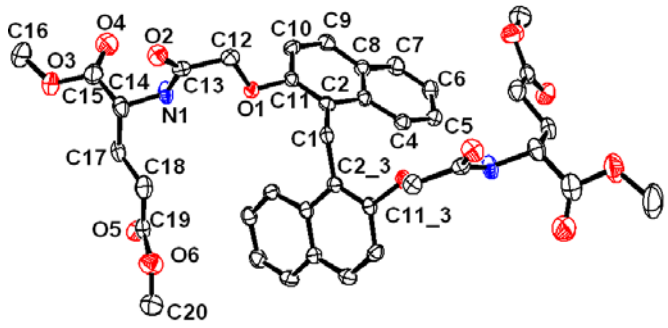


Table S02(a). Table of bond lengths (Å) and bond angles (°) for ligand L_2.

O(1)-C(11)	1.402(3)	C(17)-C(18)	1.524(4)	C(10)-H(10)	0.9300
O(1)-C(12)	1.422(3)	C(17)-H(17A)	0.9700	C(12)-C(13)	1.502(3)
O(2)-C(13)	1.239(3)	C(17)-H(17B)	0.9700	C(12)-H(12A)	0.9700
O(3)-C(15)	1.342(4)	C(18)-C(19)	1.491(4)	C(12)-H(12B)	0.9700
O(3)-C(16)	1.450(4)	C(18)-H(18A)	0.9700	C(14)-C(15)	1.512(4)
O(4)-C(15)	1.202(4)	C(18)-H(18B)	0.9700	C(14)-C(17)	1.529(4)
O(5)-C(19)	1.196(3)	C(20)-H(20A)	0.9600	C(14)-H(14)	0.9800
O(6)-C(19)	1.342(3)	C(20)-H(20B)	0.9600	C(16)-H(16A)	0.9600
O(6)-C(20)	1.455(4)	C(20)-H(20C)	0.9600	C(16)-H(16B)	0.9600
N(1)-C(13)	1.334(3)	C(7)-C(8)	1.419(4)	C(16)-H(16C)	0.9600
N(1)-C(14)	1.443(3)	C(7)-H(7)	0.9300	C(2)-C(11)	1.368(3)
N(1)-H(1N)	0.83(3)	C(8)-C(9)	1.416(4)	C(2)-C(3)	1.435(4)
C(1)-C(2)#1	1.522(3)	C(9)-C(10)	1.355(4)	C(3)-C(4)	1.422(3)
C(1)-C(2)	1.522(3)	C(9)-H(9)	0.9300	C(3)-C(8)	1.427(4)
C(1)-H(1)	0.95(2)	C(10)-C(11)	1.403(4)	C(4)-C(5)	1.368(4)
C(5)-H(5)	0.9300	C(6)-C(7)	1.365(3)	C(4)-H(4)	0.9300
C(5)-C(6)	1.398(4)	C(6)-H(6)	0.9300		

C(11)-O(1)-C(12)	118.16(19)	H(12A)-C(12)-H(12B	108.3	C(19)-C(18)-H(18B)	109.1
C(15)-O(3)-C(16)	116.1(3)	O(2)-C(13)-N(1)	123.3(3)	C(17)-C(18)-H(18B)	109.1
C(19)-O(6)-C(20)	115.7(2)	O(2)-C(13)-C(12)	120.1(2)	H(18A)-C(18)-H(18B)	107.9
C(13)-N(1)-C(14)	122.7(2)	N(1)-C(13)-C(12)	116.6(2)	O(5)-C(19)-O(6)	122.8(3)
C(13)-N(1)-H(1N)	116.4(18)	N(1)-C(14)-C(15)	111.0(3)	O(5)-C(19)-C(18)	125.6(3)
C(14)-N(1)-H(1N)	120.5(18)	N(1)-C(14)-C(17)	111.2(2)	O(6)-C(19)-C(18)	111.7(2)
C(2)#1-C(1)-C(2)	120.8(3)	C(15)-C(14)-C(17)	110.9(2)	O(6)-C(20)-H(20A)	109.5
C(2)#1-C(1)-H(1)	106.9(13)	N(1)-C(14)-H(14)	107.9	O(6)-C(20)-H(20B)	109.5
C(2)-C(1)-H(1)	108.9(13)	C(15)-C(14)-H(14)	107.9	H(20A)-C(20)-H(20B)	109.5
C(11)-C(2)-C(3)	117.6(2)	C(17)-C(14)-H(14)	107.9	O(6)-C(20)-H(20C)	109.5
C(11)-C(2)-C(1)	120.2(2)	O(4)-C(15)-O(3)	123.6(3)	H(20A)-C(20)-H(20C)	109.5
C(3)-C(2)-C(1)	122.1(2)	O(4)-C(15)-C(14)	126.6(3)	H(20B)-C(20)-H(20C)	109.5
C(4)-C(3)-C(8)	117.4(2)	O(3)-C(15)-C(14)	109.8(3)	C(10)-C(9)-C(8)	120.3(3)
C(4)-C(3)-C(2)	123.1(2)	O(3)-C(16)-H(16A)	109.5	C(10)-C(9)-H(9)	119.8
C(8)-C(3)-C(2)	119.5(2)	O(3)-C(16)-H(16B)	109.5	C(8)-C(9)-H(9)	119.8
C(5)-C(4)-C(3)	121.1(3)	H(16A)-C(16)-H(16B)	109.5	C(9)-C(10)-C(11)	120.0(2)
C(5)-C(4)-H(4)	119.5	O(3)-C(16)-H(16C)	109.5	C(9)-C(10)-H(10)	120.0
C(3)-C(4)-H(4)	119.5	H(16A)-C(16)-H(16C)	109.5	C(11)-C(10)-H(10)	120.0
C(4)-C(5)-C(6)	121.4(2)	H(16B)-C(16)-H(16C)	109.5	C(2)-C(11)-O(1)	118.2(2)
C(4)-C(5)-H(5)	119.3	C(18)-C(17)-C(14)	112.7(2)	C(2)-C(11)-C(10)	123.0(2)
C(6)-C(5)-H(5)	119.3	C(18)-C(17)-H(17A)	109.1	O(1)-C(11)-C(10)	118.5(2)
C(7)-C(6)-C(5)	119.3(3)	C(14)-C(17)-H(17A)	109.1	O(1)-C(12)-C(13)	108.8(2)
C(7)-C(6)-H(6)	120.3	C(18)-C(17)-H(17B)	109.1	O(1)-C(12)-H(12A)	109.9
C(5)-C(6)-H(6)	120.3	C(14)-C(17)-H(17B)	109.1	C(13)-C(12)-H(12A)	109.9
C(6)-C(7)-C(8)	121.3(3)	H(17A)-C(17)-H(17B)	107.8	O(1)-C(12)-H(12B)	109.9
C(6)-C(7)-H(7)	119.4	C(19)-C(18)-C(17)	112.3(2)	C(13)-C(12)-H(12B)	109.9
C(8)-C(7)-H(7)	119.4	C(19)-C(18)-H(18A)	109.1	C(9)-C(8)-C(3)	119.2(2)
C(9)-C(8)-C(7)	121.4(3)	C(17)-C(18)-H(18A)	109.1	C(7)-C(8)-C(3)	119.4(2)

Symmetry transformations used to generate equivalent atoms:
#1 x,-y,-z+2

Table S02(b). Table of torsion angles (°) for ligand **L_2**.

C(2)#1-C(1)-C(2)-C(11)	121.9(2)	N(1)-C(14)-C(17)-C(18)	58.9(3)
C(2)#1-C(1)-C(2)-C(3)	-61.6(2)	C(15)-C(14)-C(17)-C(18)	-177.2(2)
C(11)-C(2)-C(3)-C(4)	-179.0(2)	C(14)-C(17)-C(18)-C(19)	-176.6(2)
C(1)-C(2)-C(3)-C(4)	4.4(4)	C(20)-O(6)-C(19)-O(5)	0.5(4)
C(11)-C(2)-C(3)-C(8)	-0.2(4)	C(20)-O(6)-C(19)-C(18)	-179.0(2)
C(1)-C(2)-C(3)-C(8)	-176.8(2)	C(17)-C(18)-C(19)-O(5)	23.0(4)
C(8)-C(3)-C(4)-C(5)	-4.1(4)	C(17)-C(18)-C(19)-O(6)	-157.5(2)
C(2)-C(3)-C(4)-C(5)	174.7(2)	C(12)-O(1)-C(11)-C(10)	-68.3(3)
C(3)-C(4)-C(5)-C(6)	0.9(4)	C(9)-C(10)-C(11)-C(2)	4.5(4)
C(4)-C(5)-C(6)-C(7)	1.9(4)	C(9)-C(10)-C(11)-O(1)	-168.4(2)
C(5)-C(6)-C(7)-C(8)	-1.4(4)	C(11)-O(1)-C(12)-C(13)	160.7(2)
C(6)-C(7)-C(8)-C(9)	178.8(3)	C(14)-N(1)-C(13)-O(2)	-2.5(4)
C(6)-C(7)-C(8)-C(3)	-2.0(4)	C(14)-N(1)-C(13)-C(12)	177.6(2)
C(4)-C(3)-C(8)-C(9)	-176.2(2)	O(1)-C(12)-C(13)-O(2)	155.1(2)
C(2)-C(3)-C(8)-C(9)	5.0(4)	O(1)-C(12)-C(13)-N(1)	-25.0(3)
C(4)-C(3)-C(8)-C(7)	4.6(4)	C(13)-N(1)-C(14)-C(15)	91.6(3)
C(2)-C(3)-C(8)-C(7)	-174.2(2)	C(13)-N(1)-C(14)-C(17)	-144.5(3)
C(7)-C(8)-C(9)-C(10)	174.0(3)	C(16)-O(3)-C(15)-O(4)	-1.0(5)
C(3)-C(8)-C(9)-C(10)	-5.2(4)	C(16)-O(3)-C(15)-C(14)	179.5(3)

C(8)-C(9)-C(10)-C(11)	0.6(4)	N(1)-C(14)-C(15)-O(4)	12.4(4)
C(3)-C(2)-C(11)-O(1)	168.3(2)	C(17)-C(14)-C(15)-O(4)	-111.7(3)
C(1)-C(2)-C(11)-O(1)	-15.0(3)	N(1)-C(14)-C(15)-O(3)	-168.2(2)
C(3)-C(2)-C(11)-C(10)	-4.6(4)	C(17)-C(14)-C(15)-O(3)	67.7(3)
C(1)-C(2)-C(11)-C(10)	172.1(2)	C(12)-O(1)-C(11)-C(2)	118.4(2)

Symmetry transformations used to generate equivalent atoms:
#1 x,-y,-z+2

S03. Fluorescence titration studies of $\mathbf{L_1}$-$\mathbf{L_7}$ with metal ions

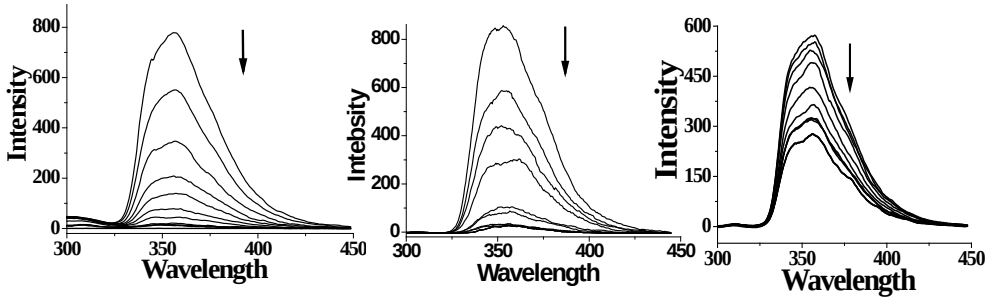


Figure S03(a). Fluorescence spectral traces obtained during the titration of L with Cu^{2+}in aqueous acetonitrile solution (1:1): (a) for $\mathbf{L_7}$; (b) for $\mathbf{L_6}$; (c) for $\mathbf{L_5}$.

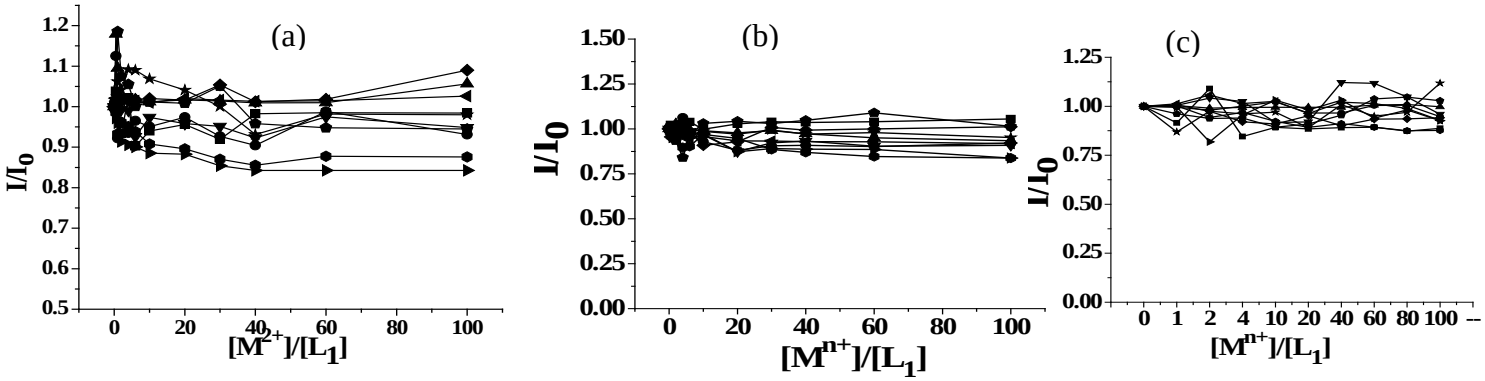


Figure S03(b). Plot of relative fluorescence intensity as a function of mole ratio of metal ion to the ligand concentration in different solvent systems. This is done for all the metal ions for which the titrations were carried out. (a) in CH_3OH; (b) in CH_3CN; (c) and CH_3CN: H_2O (1:1). The symbols correspond to, ■=Na^+; ●=K^+; ▲=Mg^{2+}; ▼=Ca^{2+}; ◀=Mn^{2+}; ▶= Fe^{2+}; ◆=Co^{2+}; ⬟=Ni^{2+}; ⬢=Cu^{2+} and ★=Zn^{2+}.

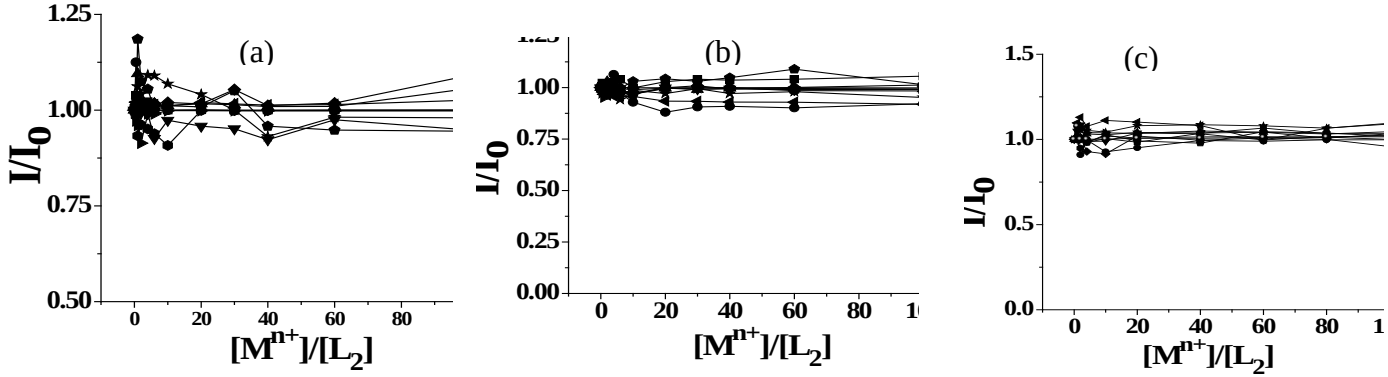


Figure S03(c). Plot of relative fluorescence intensity as a function of mole ratio of metal ion to the ligand concentration in different solvent systems. (a) in CH_3OH; (b) in CH_3CN; (c) and CH_3CN: H_2O (1:1). The symbols carry same meaning as that given in **Figure S3(b)**.

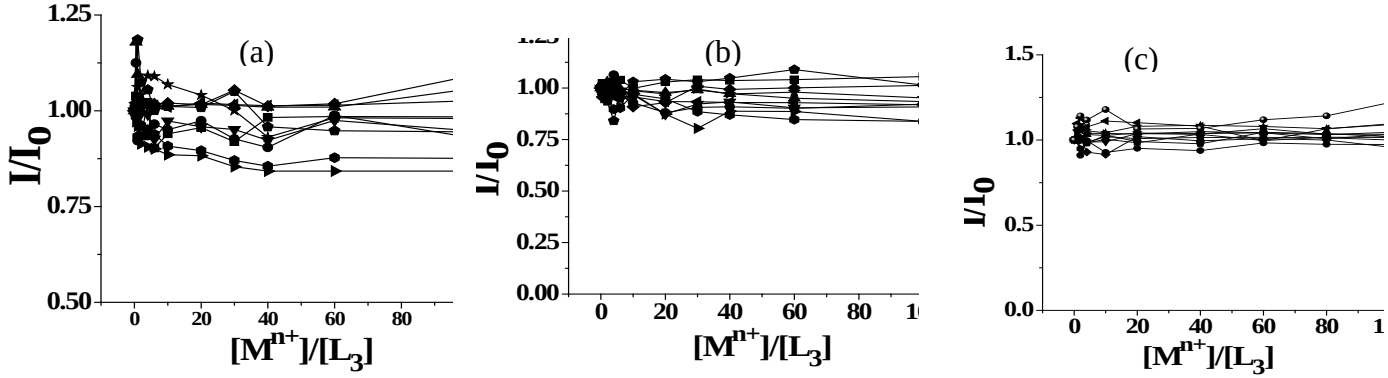


Figure S03(d). Plot of relative fluorescence intensity as a function of mole ratio of metal ion to the ligand concentration in different solvent systems. (a) in CH_3OH; (b) in CH_3CN; (c) and CH_3CN: H_2O (1:1). The symbols carry same meaning as that given in **Figure S3(b)**.

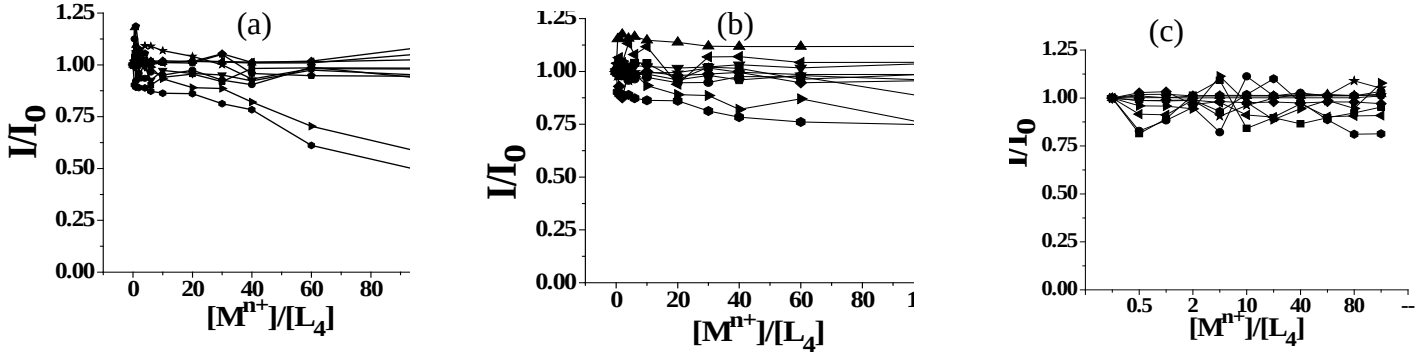


Figure S03(e). Plot of relative fluorescence intensity as a function of mole ratio of metal ion to the ligand concentration in different solvent systems. (a) in CH_3OH; (b) in CH_3CN; (c) and CH_3CN: H_2O (1:1). The symbols carry same meaning as that given in **Figure S3(b)**.

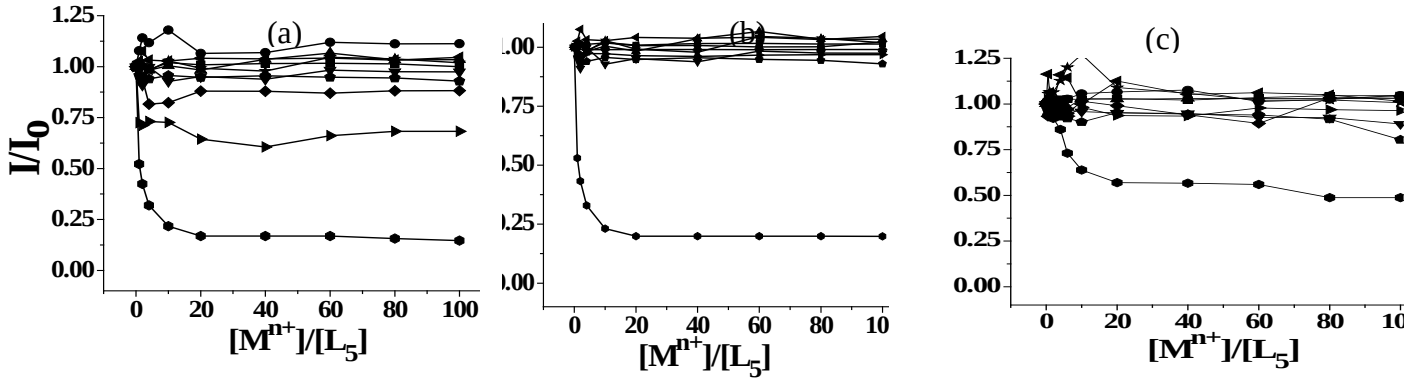


Figure S03(f). Plot of relative fluorescence intensity as a function of mole ratio of metal ion to the ligand concentration in different solvent systems. (a) in CH_3OH; (b) in CH_3CN; (c) and CH_3CN: H_2O (1:1). The symbols carry same meaning as that given in **Figure S3(b)**.

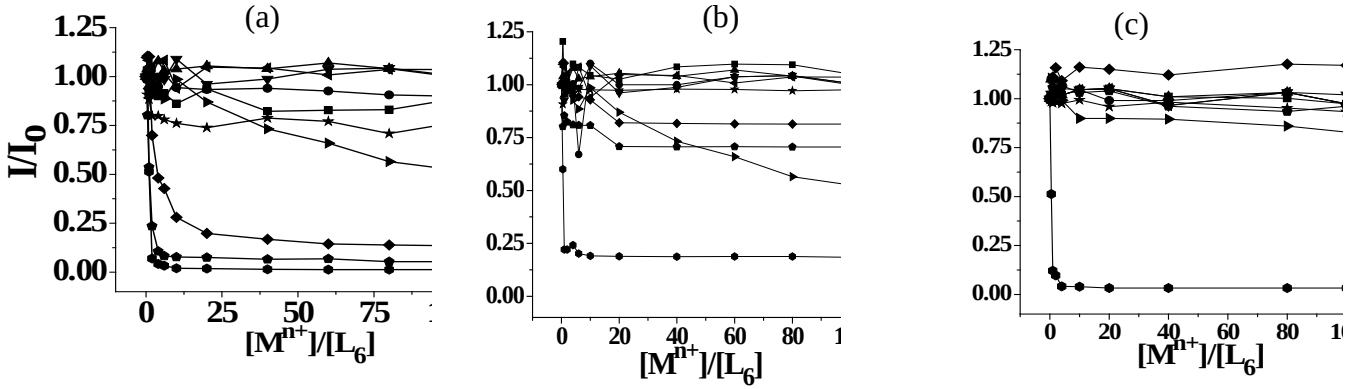


Figure S03(g). Plot of relative fluorescence intensity as a function of mole ratio of metal ion to the ligand concentration in different solvent systems. (a) in CH_3OH; (b) in CH_3CN; (c) and CH_3CN: H_2O (1:1). The symbols carry same meaning as that given in **Figure S3(b)**.

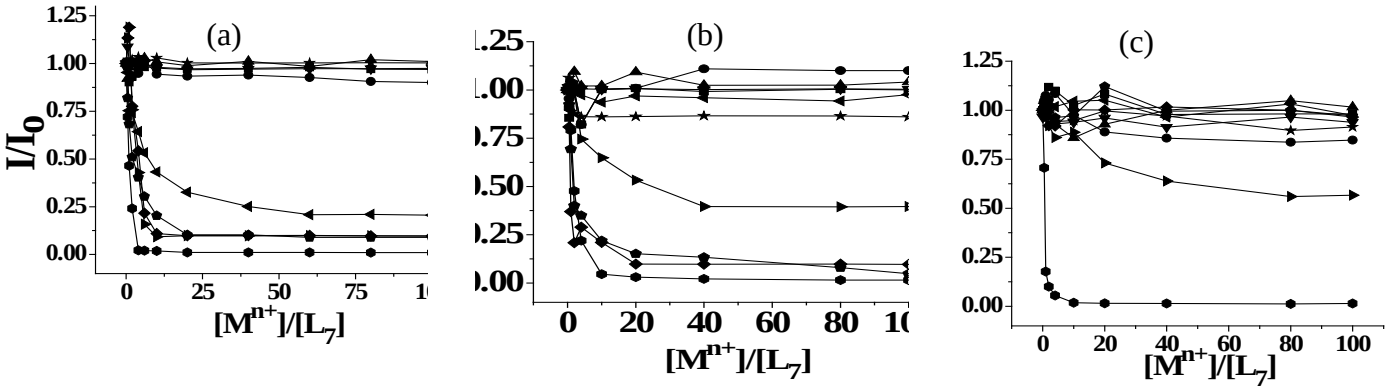


Figure S03(h). Plot of relative fluorescence intensity as a function of mole ratio of metal ion to the ligand concentration in different solvent systems. (a) in CH_3OH; (b) in CH_3CN; (c) and CH_3CN: H_2O (1:1). The symbols carry same meaning as that given in **Figure S3(b)**.

S04. Control fluorescence titration studies

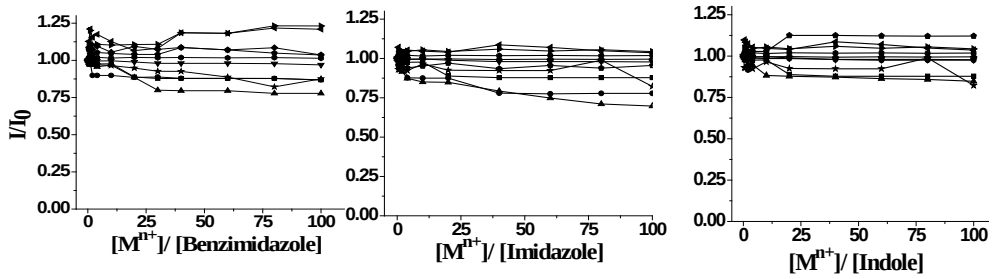


Figure S04. Plots of relative fluorescence intensity (I/I_0) *vs*. [M^{n+}]/[Control molecules] mole ratios: (a) Titration of benzimidazole by M^{n+}; (b) Titration of imidazole by M^{n+}; (c) Titration of indole by M^{n+};. The symbols correspond to, ■=Na^{+}; ●=K^{+}; ▲=Mg^{2+}; ▼=Ca^{2+}; ◀=Mn^{2+}; ▶= Fe^{2+}; ◆=Co^{2+}; ⬟=Ni^{2+}; ⬢=Cu^{2+} and ★=Zn^{2+}.

S05. Minimum detection limit experiment

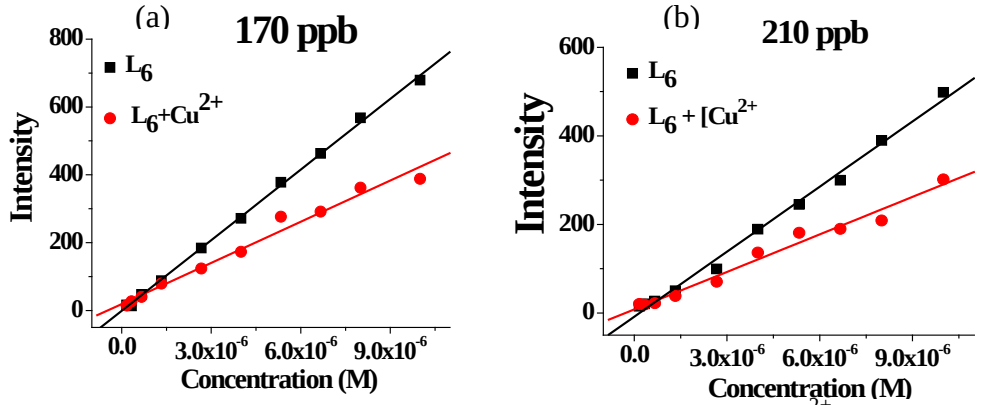


Figure S05(a). Dilution experiments carried out by keeping the [Cu^{2+}]/[$\mathbf{L_6}$] mole ratio at 1:1: (a) in methanol (b) in aqueous acetonitrile.

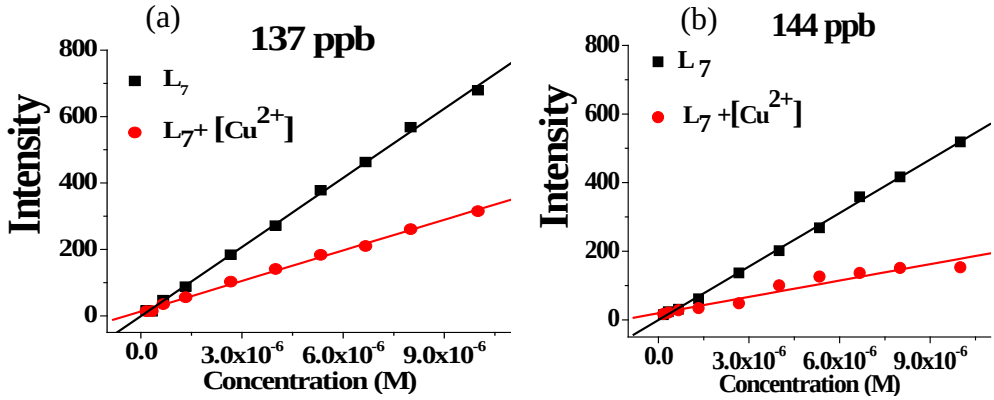


Figure S05(b). Dilution experiments carried out by keeping the [Cu^{2+}]/[$\mathbf{L_7}$] mole ratio at 1:1: (a) in methanol (b) in aqueous acetonitrile.

S06. Absorption titration studies

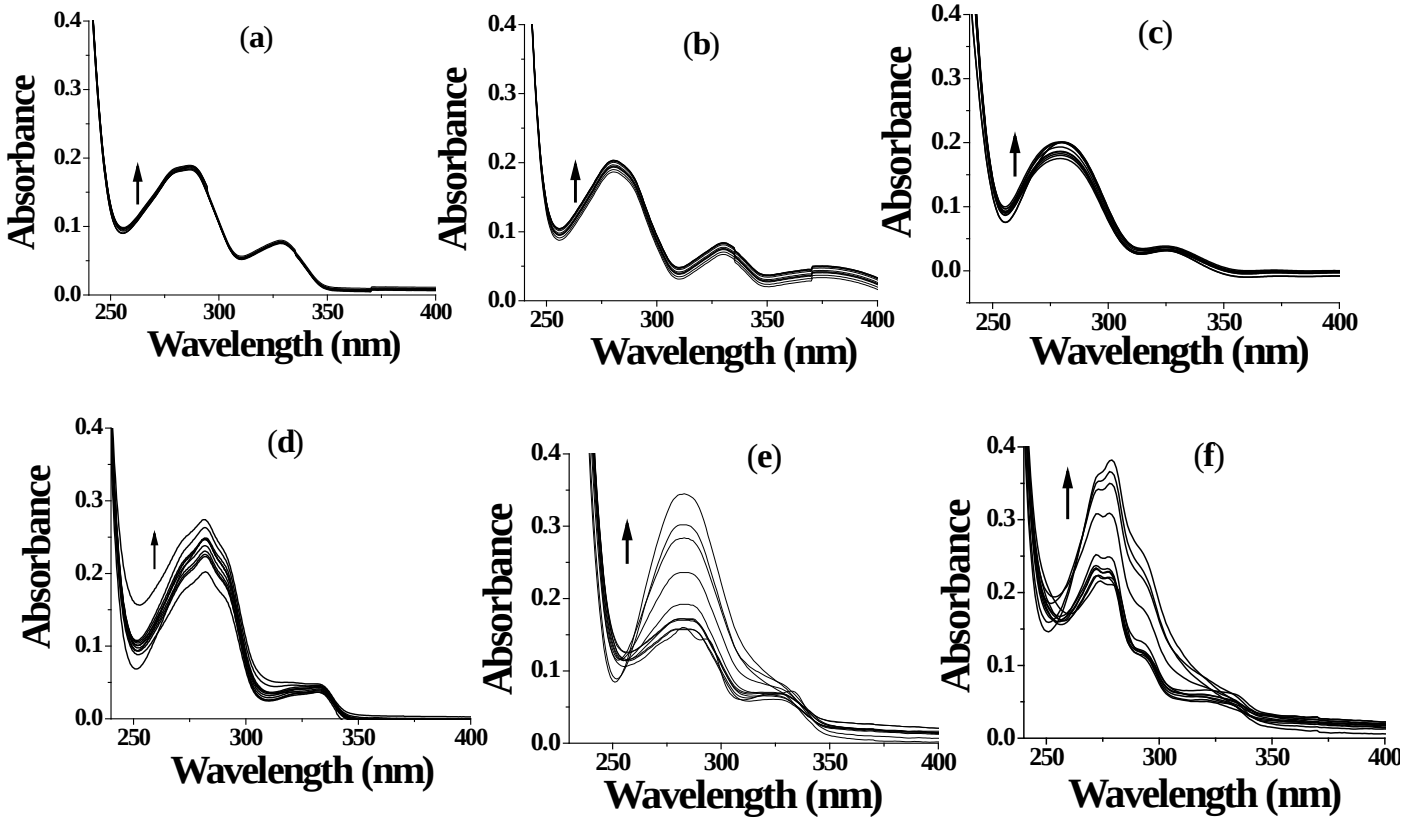
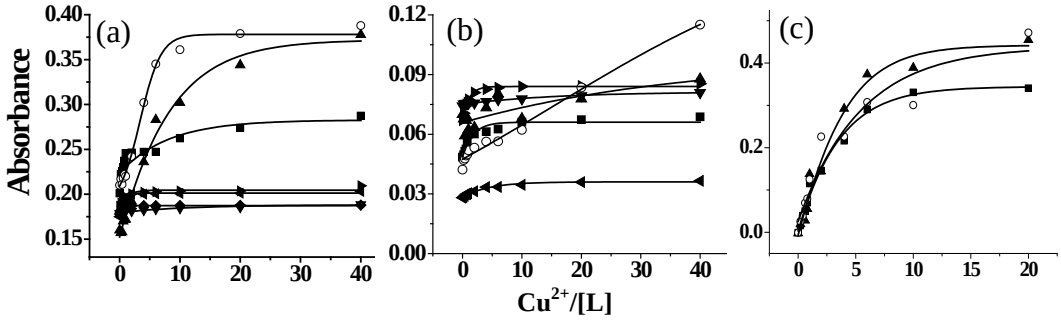


Figure S06. Absorption spectral traces for the titration of L_1 – L_7 with Cu^{2+} in 50% aqueous acetonitrile: (a) L_1, (b) L_3, (c) L_4**,** (d) L_5 , (e) L_6, and (f) L_7 .



Titration of L with Cu^{2+} in 50% aqueous acetonitrile: Plot of absorbance *vs.* mole ratio of [Cu2+]/[L] for (a) 280 nm band, (b) for 330 nm band (c) for 820 nm band. The symbols correspond to, B = L_1; Λ = L_2; β = L_3; Ω = L_4; ■ = L_5; 7 = L_6; and ○ = L_7.

S07. Job's plots

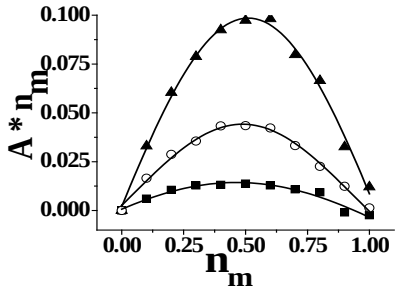


Figure S07. Job's plots for the titration of **L** with Cu^{2+} in aqueous acetonitrile where n_m is mole fraction of the metal ion added and A is absorbance. The symbols correspond to, ■ = $\mathbf{L_5}$, ▲ = $\mathbf{L_6}$ and ○ = $\mathbf{L_7}$.

S08. Mass spectral studies of L_6 and L_7 with Cu^{2+}

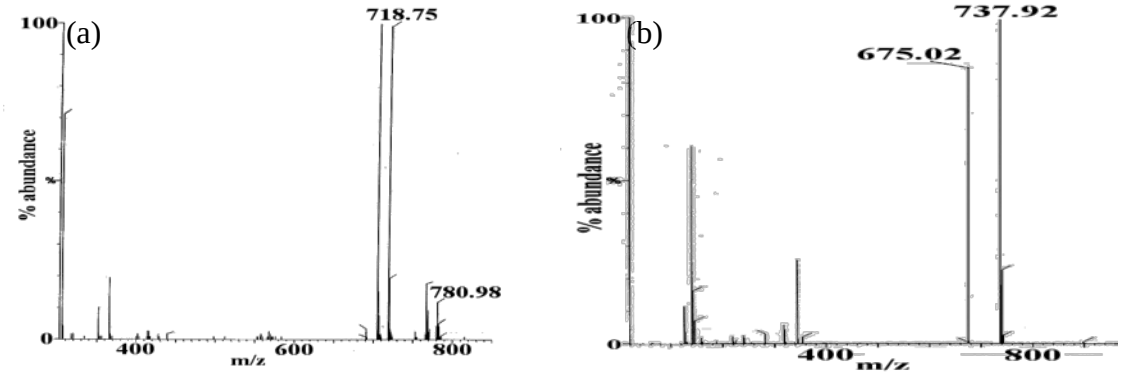


Figure S08. ESI mass spectrum showing the molecular ion peak for 1:1 complex formed between Cu^{2+} and $\mathbf{L_6}$ (a) & Cu^{2+} and $\mathbf{L_7}$ (b).

S09. Competitive metal ion titrations

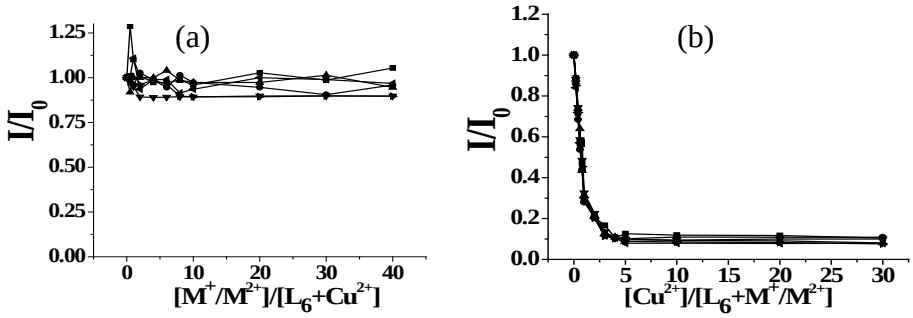


Figure S09(a). Plots of relative fluorescence intensity (I/I_0): (a) Titration of {L_6 + 5 equivalents Cu^{2+}} by M^{2+}; (b) Titration of {L_6 + equivalents M^{2+}} by Cu^{2+}. The symbols correspond to, ■=Na^+; ●=K^+; ▲=Mg^{2+}; ▼=Ca^{2+}; ◄=Cu^{2+}; ►= Zn^{2+}.

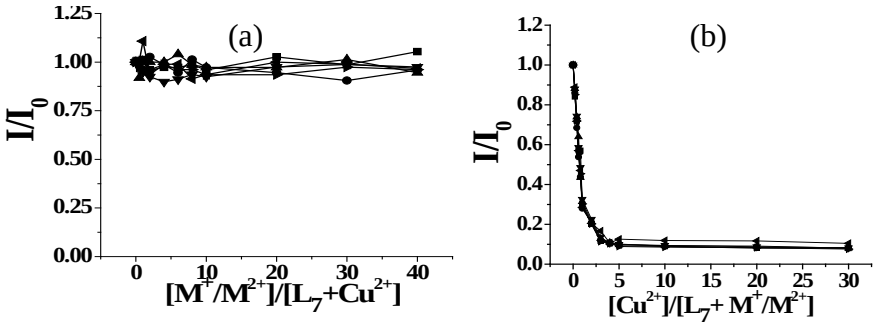


Figure S09(b). Plots of relative fluorescence intensity (I/I_0): (a) Titration of {L_7 + 5 equivalents Cu^{2+}} by M^{2+}; (b) Titration of {L_7 + equivalents M^{2+}} by Cu^{2+}. The symbols correspond to, ■=Na^+; ●=K^+; ▲=Mg^{2+}; ▼=Ca^{2+}; ◄=Cu^{2+}; ►= Zn^{2+}.

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S10. ^{1}H NMR titration studies

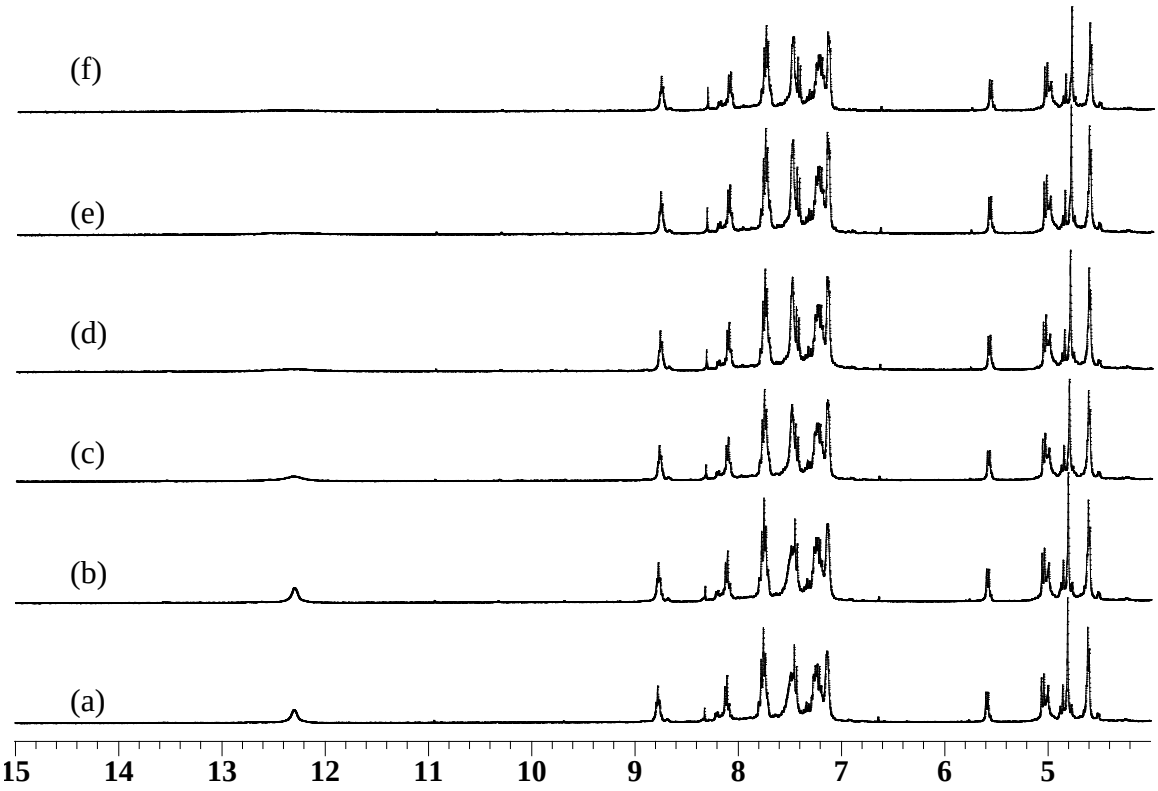

Figure S10. ^{1}H NMR spectra measured during the titration of L_7 with different mole ratios of Zn^{2+}(in DMSO-d_6): (a) 0, (b) 0.02, (c) 0.04, (d) 0.08, (e) 0.1 and (f) 0.2.

S11. Computational studies

All the calculations were performed by using Gaussian 03 package. The initial guess for the structure of L_6 was obtained by appropriately modifying the crystal structure of L_2 of ***mbn*** and optimizing the same in a cascade fashion starting from AM1 → HF/3-21G → HF/6-31G. In order to bring both the arms on the same side to form a binding core, appropriate changes were made in the dihedral angles of the arms of L_6 to mimic the dipicolyl derivative present in the crystal structure of its copper complex that was reported by us recently, and the model was optimized in HF/6-31G. At this stage, Cu^{2+} was placed away from the binding core (5 Å) of the optimized structure of **L_6** so that there are no interactions present between **L_6** and Cu^{2+} in the initial guess structure. This optimization has been carried out by DFT methods using B3LYP/3-21g* initially and the resultant structure was further optimized by B3LYP/6-31g*. The resultant structure has been further subjected to the interaction with one acetonitrile molecule. Further optimization carried out in presence of acetonitrile in B3LYP/6-31g*

(a) Cartesian coordinates of **L_6** as obtained from HF/6-31G level of optimization

Z	Cartesian Coordinates		
	x	y	z
1	-8.373639000	-1.019379000	1.855630000
1	-3.299142000	-6.106402000	-3.253501000
1	-0.874047000	-5.786668000	-3.092272000
1	-7.479328000	0.679648000	0.330020000
6	-2.886415000	-5.419693000	-2.540044000
6	-7.327887000	-0.994857000	1.617927000
6	-1.540143000	-5.240453000	-2.450897000
6	-6.830206000	-0.053489000	0.770904000
1	-6.842412000	-2.683555000	2.863350000
1	-4.805375000	-4.842760000	-1.749326000
6	-6.453383000	-1.943743000	2.190179000
6	-3.744453000	-4.697036000	-1.682786000
1	1.063022000	-4.731097000	-2.057072000
1	-5.616916000	1.723641000	-0.818069000
6	-5.448405000	-0.009343000	0.449622000
6	-0.983535000	-4.335703000	-1.509907000
6	0.420909000	-4.172280000	-1.403280000
6	-4.942681000	0.992673000	-0.415072000
6	-5.121329000	-1.927826000	1.899768000

6	-3.238232000	-3.815298000	-0.774365000
6	-1.838163000	-3.594833000	-0.657078000
6	-4.561627000	-0.962300000	1.012690000
1	-4.493406000	-2.661462000	2.360082000
1	-3.912154000	-3.279380000	-0.143472000
6	0.942790000	-3.323106000	-0.482986000
6	-3.618470000	1.051379000	-0.705675000
1	-3.222042000	1.845299000	-1.307672000
1	2.002015000	-3.185591000	-0.385418000
6	-1.279013000	-2.678123000	0.298523000
6	-3.166557000	-0.915738000	0.670184000
6	4.918021000	0.624288000	0.850874000
6	1.238713000	4.257335000	-0.280274000
1	5.963104000	0.869067000	0.981775000
1	1.641828000	5.224961000	-0.549578000
1	6.533774000	-4.296606000	0.519024000
1	-2.336455000	7.015271000	-0.398816000
6	0.083677000	-2.588032000	0.365046000
6	-2.745342000	0.087606000	-0.157008000
1	2.646089000	-0.753624000	0.812533000
1	-0.712162000	2.299583000	-0.201937000

8	-2.179625000	4.522169000	-1.518057000
8	6.610602000	-1.592616000	0.264770000
6	-2.140422000	-1.874795000	1.265165000
8	-1.386093000	0.199110000	-0.399592000
8	0.692405000	-1.717507000	1.268990000
6	-1.026216000	4.828056000	-1.314031000
6	5.489017000	-1.819272000	0.689162000
6	-1.626213000	7.160525000	-1.196706000
6	5.629811000	-4.111734000	-0.037599000
1	4.959750000	-4.948942000	0.025796000
1	-1.072870000	8.071870000	-1.058491000
7	3.272158000	-1.096724000	1.507842000
7	-0.320671000	2.526734000	-1.089750000
6	0.148509000	3.871171000	-1.287693000
6	4.673800000	-0.779309000	1.438894000
8	4.903772000	-3.006295000	0.557167000
8	-0.635898000	6.107420000	-1.169217000
1	-2.632353000	-2.572936000	1.926544000
1	-1.469523000	-1.288730000	1.874494000
1	-2.139069000	7.160804000	-2.145086000
1	5.870009000	-3.882661000	-1.063150000
1	-1.604491000	0.008794000	-2.463389000
1	1.242369000	-3.306809000	2.499470000

1	0.589559000	3.912299000	-2.276096000
1	5.060814000	-0.795332000	2.451290000
6	1.325044000	-2.230375000	2.444717000
6	-0.853253000	0.249715000	-1.724329000
6	-0.274988000	1.601985000	-2.050352000
6	2.788322000	-1.873326000	2.493453000
1	0.840138000	-1.801229000	3.309219000
1	-0.061732000	-0.480381000	-1.781804000
8	3.474671000	-2.288243000	3.427733000
8	0.215531000	1.787055000	-3.171855000
1	4.329989000	1.326920000	1.422562000
1	2.028727000	3.519894000	-0.370814000
6	0.737301000	4.292153000	1.123568000
7	-0.431337000	3.871728000	1.526401000
6	-0.481848000	4.074258000	2.898592000
6	0.681024000	4.624004000	3.316714000
7	1.458985000	4.761656000	2.177938000
1	-1.341138000	3.808959000	3.467006000
1	1.020603000	4.922022000	4.280293000
1	2.372415000	5.140689000	2.137328000
6	4.537228000	0.757744000	-0.585455000
7	5.343313000	0.390143000	-1.618640000
6	4.657608000	0.632770000	-2.792295000
6	3.455210000	1.138346000	-2.423163000
7	3.394983000	1.211301000	-1.036580000
1	6.242276000	-0.018380000	-1.521349000
1	5.074366000	0.428927000	-3.750129000
1	2.633289000	1.440616000	-3.028901000

(b) Cartesian coordinates of $[Cu(\mathbf{L_6})]^{2+}$ as obtained from B3LYP/6-31G* level of optimisation.

Z	Cartesian coordinates		
	x	y	z
1	9.195723000	-1.116709000	-2.162950000
1	4.069951000	-3.754648000	4.500673000
1	1.778346000	-4.344579000	3.762055000
1	8.536673000	1.007581000	-1.074432000
6	3.693364000	-3.410043000	3.542174000
6	8.158539000	-0.932939000	-1.899938000
6	2.421410000	-3.733184000	3.133420000
6	7.792246000	0.247627000	-1.297001000
1	7.470008000	-2.850928000	-2.635966000
1	5.542440000	-2.422752000	2.985718000

6	7.177564000	-1.913992000	-2.170924000
6	4.524279000	-2.650486000	2.683147000
1	0.020751000	-4.307760000	2.098396000
1	6.835989000	2.443276000	-0.075838000
6	6.439011000	0.500890000	-0.948151000
6	1.923547000	-3.305537000	1.870223000
6	0.629392000	-3.684822000	1.448326000
6	6.067533000	1.710423000	-0.305851000
6	5.855173000	-1.697450000	-1.848863000
6	4.068672000	-2.209397000	1.460891000
6	2.746573000	-2.496962000	1.003431000
6	5.432071000	-0.482999000	-1.238566000
1	5.133933000	-2.479860000	-2.057403000
1	4.742782000	-1.653004000	0.828788000
6	0.152304000	-3.298541000	0.218001000
6	4.758535000	1.951156000	0.030382000
1	4.476973000	2.869683000	0.537159000
1	-0.833710000	-3.626009000	-0.093480000
6	2.224961000	-2.049762000	-0.257020000
6	4.059136000	-0.215756000	-0.898026000
6	-4.575535000	-1.100484000	-0.603375000
6	-2.032512000	4.888714000	-1.530193000
1	-5.651321000	-0.950084000	-0.470722000
1	-3.112722000	4.984708000	-1.675439000
1	-6.908633000	-5.393594000	-2.116676000
1	-3.542902000	3.498333000	2.784519000
6	0.953789000	-2.493645000	-0.622974000
6	3.769528000	0.990556000	-0.284191000
1	-3.015350000	-3.560386000	-2.407617000
1	0.106264000	4.330246000	-0.297602000
8	-2.647694000	1.983840000	0.755654000
8	-6.100613000	-3.451276000	-0.435343000
6	2.931345000	-1.156506000	-1.286754000
8	2.438889000	1.251107000	0.074978000
8	0.514682000	-2.090154000	-1.876903000
6	-2.615020000	3.130499000	0.306849000
6	-5.296486000	-3.422368000	-1.343905000
6	-4.162655000	3.848890000	1.957868000
6	-5.848676000	-5.633013000	-2.022061000
1	-5.523652000	-6.297408000	-2.820157000
1	-4.629625000	4.802358000	2.195691000
7	-3.062725000	-2.648847000	-1.962441000
7	-0.324839000	3.410108000	-0.533201000
6	-1.741719000	3.508361000	-0.898417000
6	-4.435045000	-2.189990000	-1.687985000

8	-5.059197000	-4.418662000	-2.193262000
8	-3.324021000	4.120465000	0.799193000
1	3.266259000	-1.795084000	-2.110765000
1	2.144142000	-0.537335000	-1.724074000
1	-4.911535000	3.097614000	1.701959000
1	-5.648508000	-6.066779000	-1.040963000
1	2.230630000	2.548174000	-1.533987000
1	-0.719577000	-3.714007000	-2.295212000
1	-1.940741000	2.731229000	-1.645713000
1	-4.852322000	-1.774784000	-2.617317000
6	-0.662649000	-2.622686000	-2.407900000
6	1.882646000	2.413570000	-0.498684000
6	0.367529000	2.273145000	-0.548707000
6	-1.925423000	-1.944507000	-1.851878000
1	-0.630970000	-2.399832000	-3.481544000
1	2.149566000	3.324956000	0.055482000
8	-1.877684000	-0.789239000	-1.391025000
8	-0.161674000	1.143772000	-0.692966000
1	-4.158531000	-0.167685000	-0.976820000
1	-1.581003000	4.881794000	-2.530873000
6	-1.501009000	6.057119000	-0.746992000
7	-0.329403000	6.075993000	-0.128250000

6	-0.188800000	7.341314000	0.399962000
6	-1.285111000	8.099718000	0.087000000
7	-2.113644000	7.267525000	-0.640288000
1	0.687340000	7.627213000	0.963416000
1	-1.547329000	9.123424000	0.305375000
1	-3.005565000	7.528359000	-1.038954000
6	-3.967521000	-1.416503000	0.729439000
7	-4.578462000	-2.193021000	1.651753000
6	-3.791956000	-2.261233000	2.778666000
6	-2.692528000	-1.497979000	2.506501000
7	-2.805864000	-0.977206000	1.229011000
1	-5.450896000	-2.680895000	1.469464000
1	-4.076369000	-2.827916000	3.651554000
1	-1.837561000	-1.289405000	3.127173000
29	-1.482780000	0.161959000	0.338655000
7	-0.161314000	0.125658000	1.868675000
6	0.798565000	0.136578000	2.514173000
6	2.001561000	0.157503000	3.327882000
1	1.856491000	0.810500000	4.194354000
1	2.239263000	-0.856414000	3.666398000
1	2.828403000	0.529627000	2.716023000