Electronic Supplementary Material (ESI) for Dalton Transactions

Ratiometric fluorescence *off-on-off* sensor for Cu^{2+} in aqueous buffer by a lower rim triazole linked benzimidazole conjugate of calix[4]arene

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Contents

^{1}H NMR, ^{13}C NMR and ESI MS spectra of **L**.

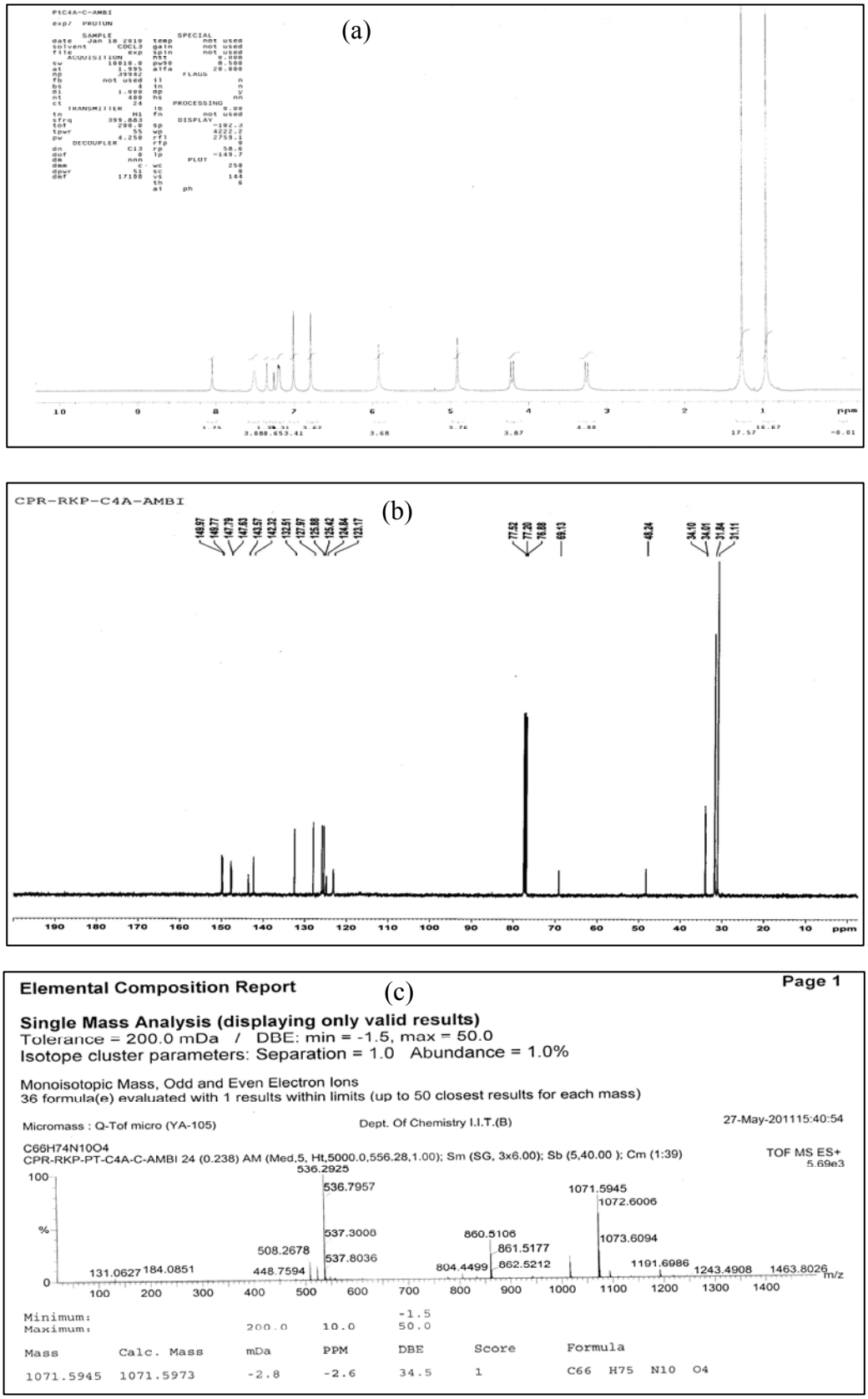


Figure S1. Spectra of **L**: (a) ^{1}H NMR; (b) ^{13}C NMR and (c) ESI HRMS.

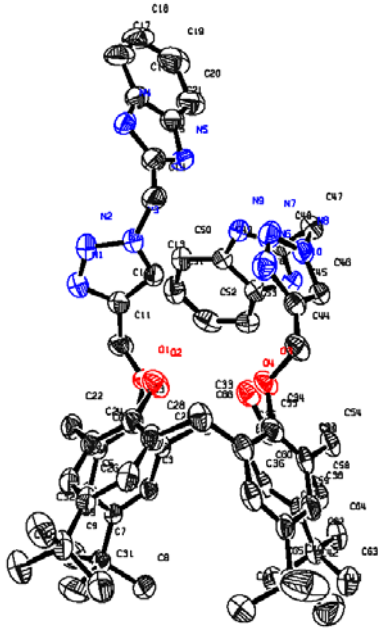


Table S1. Selected bond lengths for **L**

O(1)-C(1)	1.395(5)	C(20)-C(21)	1.370(8)	C(62)-C(63)	1.531(7)
O(1)-C(11)	1.450(5)	C(22)-C(24)	1.515(6)	C(62)-C(65)	1.544(7)
O(2)-C(23)	1.352(6)	C(23)-C(24)	1.397(6)	O(102)-C(333)	1.402(7)
O(3)-C(34)	1.397(6)	C(23)-C(28)	1.399(7)	O(103)-C(101)	1.412(11)
O(3)-C(44)	1.440(5)	C(24)-C(25)	1.396(7)	C(102)-O(101)	1.437(8)
O(4)-C(55)	1.381(5)	C(25)-C(26)	1.388(7)	C(55)-C(57)	1.388(6)
N(1)-N(2)	1.315(6)	C(26)-C(27)	1.404(6)	C(55)-C(61)	1.406(6)
N(1)-C(12)	1.354(6)	C(26)-C(29)	1.516(7)	C(57)-C(58)	1.383(6)
N(2)-N(3)	1.330(5)	C(27)-C(28)	1.399(7)	C(58)-C(59)	1.396(6)
N(3)-C(13)	1.334(5)	C(28)-C(33)	1.500(6)	C(59)-C(60)	1.413(6)
N(3)-C(14)	1.475(6)	C(29)-C(31)	1.520(7)	C(59)-C(62)	1.522(7)
N(4)-C(15)	1.308(6)	C(29)-C(32)	1.528(7)	C(60)-C(61)	1.379(6)
N(4)-C(16)	1.378(7)	C(29)-C(30)	1.525(7)	C(61)-C(66)	1.517(6)
N(5)-C(15)	1.368(7)	C(33)-C(35)	1.531(6)	C(62)-C(64)	1.522(7)
N(5)-C(21)	1.378(7)	C(34)-C(39)	1.393(6)	C(7)-C(8)	1.540(6)
N(6)-C(45)	1.378(6)	C(34)-C(35)	1.404(7)	C(11)-C(12)	1.482(7)
N(7)-N(8)	1.334(5)	C(35)-C(36)	1.381(7)	C(12)-C(13)	1.354(6)
N(8)-C(46)	1.341(6)	C(36)-C(37)	1.404(6)	C(14)-C(15)	1.490(8)
N(8)-C(47)	1.466(6)	C(37)-C(38)	1.378(7)	C(16)-C(17)	1.373(7)
N(9)-C(48)	1.337(5)	C(37)-C(40)	1.528(7)	C(16)-C(21)	1.421(8)
N(9)-C(49)	1.395(6)	C(38)-C(39)	1.387(7)	C(17)-C(18)	1.366(10)
N(10)-C(48)	1.342(6)	C(39)-C(54)	1.519(7)	C(18)-C(19)	1.427(10)
N(10)-C(56)	1.382(6)	C(40)-C(42)	1.506(9)	C(19)-C(20)	1.403(8)
C(1)-C(6)	1.386(6)	C(40)-C(41)	1.532(7)	C(52)-C(53)	1.377(7)
C(1)-C(2)	1.406(6)	C(40)-C(43)	1.565(8)	C(53)-C(56)	1.385(7)
C(2)-C(3)	1.382(6)	C(44)-C(45)	1.467(7)	C(54)-C(57)	1.515(6)
C(2)-C(66)	1.529(6)	C(45)-C(46)	1.372(7)	C(6)-C(22)	1.509(6)
C(3)-C(4)	1.392(6)	C(47)-C(48)	1.478(7)	C(7)-C(9)	1.529(7)
C(4)-C(5)	1.388(6)	C(49)-C(50)	1.385(6)	C(7)-C(10)	1.526(7)
C(4)-C(7)	1.529(6)	C(49)-C(56)	1.409(6)	C(51)-C(52)	1.408(7)
C(50)-C(51)	1.383(7)	C(5)-C(6)	1.411(6)		

Table S2. Selected bond angles for **L**

C(1)-O(1)-C(11)	114.1(3)	N(5)-C(15)-C(14)	122.6(4)	C(38)-C(39)-C(54)	119.8(4)
C(34)-O(3)-C(44)	113.7(3)	N(4)-C(16)-C(17)	129.4(6)	C(34)-C(39)-C(54)	121.1(4)
N(2)-N(1)-C(12)	109.2(4)	N(4)-C(16)-C(21)	109.6(4)	C(42)-C(40)-C(41)	108.7(5)
N(1)-N(2)-N(3)	106.5(4)	C(17)-C(16)-C(21)	121.0(6)	C(42)-C(40)-C(37)	110.7(5)
N(2)-N(3)-C(13)	111.3(4)	C(18)-C(17)-C(16)	117.0(6)	C(41)-C(40)-C(37)	110.3(4)
N(2)-N(3)-C(14)	119.5(4)	C(17)-C(18)-C(19)	122.7(6)	C(42)-C(40)-C(43)	109.9(5)
C(13)-N(3)-C(14)	129.2(4)	C(20)-C(19)-C(18)	120.3(7)	C(41)-C(40)-C(43)	104.3(5)
C(15)-N(4)-C(16)	105.0(5)	C(21)-C(20)-C(19)	115.9(6)	C(37)-C(40)-C(43)	112.6(4)
C(15)-N(5)-C(21)	106.2(4)	C(20)-C(21)-N(5)	131.7(5)	O(3)-C(44)-C(45)	107.8(4)
N(7)-N(6)-C(45)	109.0(4)	C(20)-C(21)-C(16)	123.1(5)	C(46)-C(45)-N(6)	107.1(4)
N(6)-N(7)-N(8)	107.5(4)	N(5)-C(21)-C(16)	105.2(5)	C(46)-C(45)-C(44)	129.7(4)
N(7)-N(8)-C(46)	111.2(4)	C(24)-C(22)-C(6)	111.8(3)	N(6)-C(45)-C(44)	123.2(5)
N(7)-N(8)-C(47)	119.5(4)	O(2)-C(23)-C(24)	123.8(4)	N(8)-C(46)-C(45)	105.2(4)
C(46)-N(8)-C(47)	128.8(4)	O(2)-C(23)-C(28)	115.7(4)	N(8)-C(47)-C(48)	109.8(4)
C(48)-N(9)-C(49)	104.5(4)	C(24)-C(23)-C(28)	120.4(5)	N(9)-C(48)-N(10)	112.9(4)
C(48)-N(10)-C(56)	108.1(4)	C(25)-C(24)-C(23)	118.4(4)	N(9)-C(48)-C(47)	123.2(4)
C(6)-C(1)-O(1)	117.9(4)	C(25)-C(24)-C(22)	120.1(4)	N(10)-C(48)-C(47)	123.6(4)
C(6)-C(1)-C(2)	122.2(4)	C(23)-C(24)-C(22)	121.5(4)	C(50)-C(49)-N(9)	129.7(4)
O(1)-C(1)-C(2)	119.7(4)	C(26)-C(25)-C(24)	123.7(4)	C(50)-C(49)-C(56)	120.6(4)
C(3)-C(2)-C(1)	117.1(4)	C(25)-C(26)-C(27)	115.9(5)	N(9)-C(49)-C(56)	109.7(4)
C(3)-C(2)-C(66)	120.3(4)	C(25)-C(26)-C(29)	124.0(4)	C(51)-C(50)-C(49)	118.0(4)
C(1)-C(2)-C(66)	122.5(4)	C(27)-C(26)-C(29)	120.1(4)	C(50)-C(51)-C(52)	120.8(5)
C(2)-C(3)-C(4)	123.1(4)	C(28)-C(27)-C(26)	122.8(4)	C(53)-C(52)-C(51)	121.7(5)
C(5)-C(4)-C(3)	117.9(4)	C(27)-C(28)-C(23)	118.7(4)	C(52)-C(53)-C(56)	117.2(4)
C(5)-C(4)-C(7)	121.2(4)	C(27)-C(28)-C(33)	120.0(4)	C(57)-C(54)-C(39)	113.6(4)
C(3)-C(4)-C(7)	121.0(4)	C(23)-C(28)-C(33)	121.1(4)	N(10)-C(56)-C(53)	133.5(4)
C(4)-C(5)-C(6)	121.6(4)	C(26)-C(29)-C(31)	110.7(4)	N(10)-C(56)-C(49)	104.8(4)
C(1)-C(6)-C(5)	117.8(4)	C(26)-C(29)-C(32)	109.9(4)	C(53)-C(56)-C(49)	121.7(4)
C(1)-C(6)-C(22)	122.3(4)	C(31)-C(29)-C(32)	108.2(5)	O(4)-C(55)-C(57)	123.4(4)
C(5)-C(6)-C(22)	119.7(4)	C(26)-C(29)-C(30)	112.7(4)	O(4)-C(55)-C(61)	115.5(4)
C(4)-C(7)-C(9)	108.4(4)	C(31)-C(29)-C(30)	107.5(4)	C(57)-C(55)-C(61)	121.1(4)
C(4)-C(7)-C(10)	111.9(4)	C(32)-C(29)-C(30)	107.6(4)	C(58)-C(57)-C(55)	118.3(4)
C(9)-C(7)-C(10)	109.2(4)	C(28)-C(33)-C(35)	109.8(4)	C(58)-C(57)-C(54)	119.0(4)
C(4)-C(7)-C(8)	110.3(4)	C(39)-C(34)-O(3)	119.2(4)	C(55)-C(57)-C(54)	122.7(4)
C(9)-C(7)-C(8)	109.4(4)	C(39)-C(34)-C(35)	120.9(4)	C(57)-C(58)-C(59)	123.7(4)
C(10)-C(7)-C(8)	107.6(4)	O(3)-C(34)-C(35)	119.7(4)	C(58)-C(59)-C(60)	115.6(4)
O(1)-C(11)-C(12)	107.2(4)	C(36)-C(35)-C(34)	117.5(4)	C(58)-C(59)-C(62)	124.3(4)
N(1)-C(12)-C(13)	107.8(4)	C(36)-C(35)-C(33)	120.3(4)	C(60)-C(59)-C(62)	120.1(4)
N(1)-C(12)-C(11)	122.1(4)	C(34)-C(35)-C(33)	122.0(4)	C(61)-C(60)-C(59)	123.0(4)
C(13)-C(12)-C(11)	130.0(4)	C(35)-C(36)-C(37)	123.2(5)	C(60)-C(61)-C(55)	118.3(4)
N(3)-C(13)-C(12)	105.3(4)	C(38)-C(37)-C(36)	117.0(4)	C(60)-C(61)-C(66)	120.8(4)
N(3)-C(14)-C(15)	109.3(4)	C(38)-C(37)-C(40)	123.2(4)	C(55)-C(61)-C(66)	120.8(4)
N(4)-C(15)-N(5)	114.0(5)	C(36)-C(37)-C(40)	119.7(4)	C(59)-C(62)-C(64)	109.9(4)
N(4)-C(15)-C(14)	123.5(5)	C(37)-C(38)-C(39)	122.4(4)	C(59)-C(62)-C(63)	112.1(4)
C(63)-C(62)-C(65)	107.1(4)	C(38)-C(39)-C(34)	119.0(4)	C(64)-C(62)-C(63)	108.6(4)
C(61)-C(66)-C(2)	109.2(4)	C(64)-C(62)-C(65)	109.3(4)	C(59)-C(62)-C(65)	109.8(3)

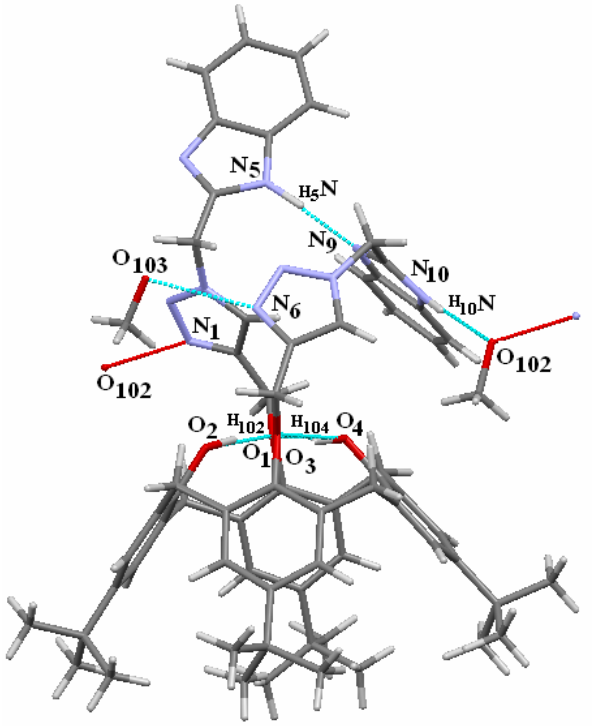


Figure S2: Schematic diagram shows the hydrogen bonding pattern for **L**.

Table S3. Hydrogen bond length and bond angle data for **L**.

D – H ··· A	D – H (Å)	A ··· H (Å)	D ··· A (Å)	D – H – A (°)
O4 – H104…O3	1.05 (7)	1.67 (7)	2.706 (4)	165 (6)
O2 – H102 …O1	1.02 (6)	1.70 (7)	2.712 (4)	167 (5)
N10 – H10N …O102	0.80 (4)	1.96 (4)	2.755 (4)	175 (5)
N5 – H5N … N9	1.07 (3)	1.79 (3)	2.857 (4)	171 (4)

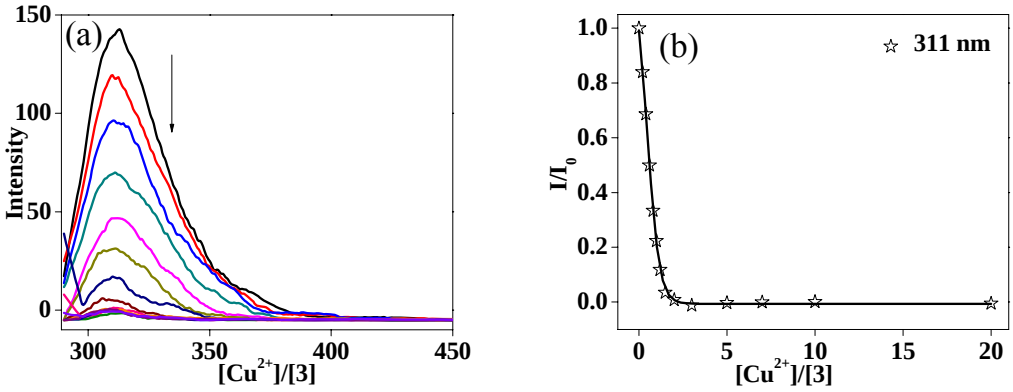


Figure S3: (a) Fluorescence spectra obtained during the titration of control molecule **3** in methanol. (b) relative fluorescence intensity (I/I_0) as a function of [Cu^{2+}]/[**3**] mole ratio.

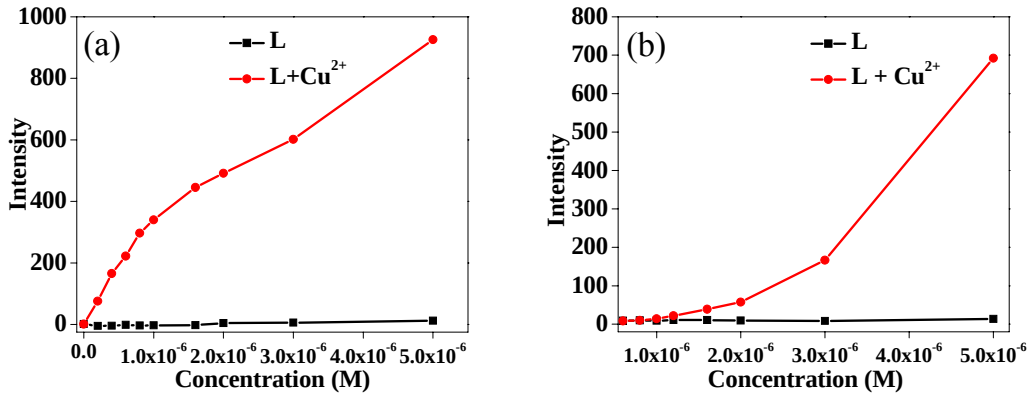


Figure S4: Fluorescence spectra obtained during the titration of **L** in (a) methanol and (b) aqueous-buffer medium by keeping ligand to Zn^{2+} ratio as 1:1. This is used for obtaining the minimum detection of limit of Cu^{2+} by **L**.

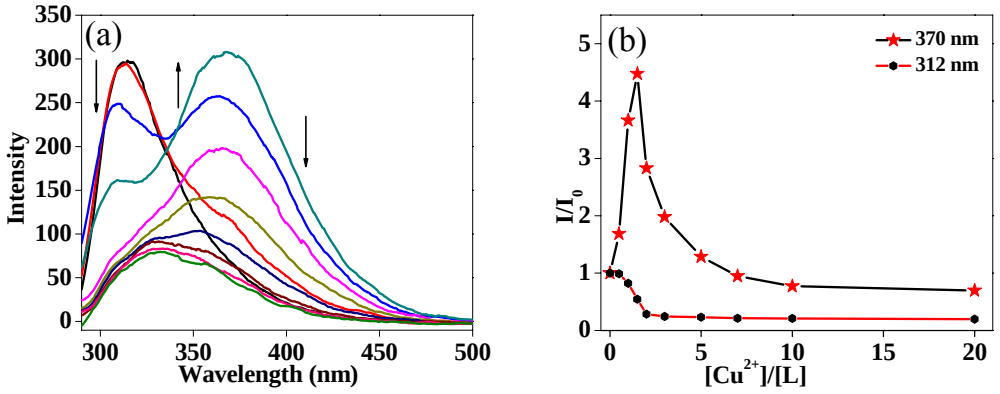


Figure S5: (a) Fluorescence spectra obtained during the titration of **L** with Cu^{2+} in ethanol; λ_{ex} = 280 nm; (b) relative fluorescence intensity (I/I_0) as a function of [Cu^{2+}]/[**L**] mole ratio.

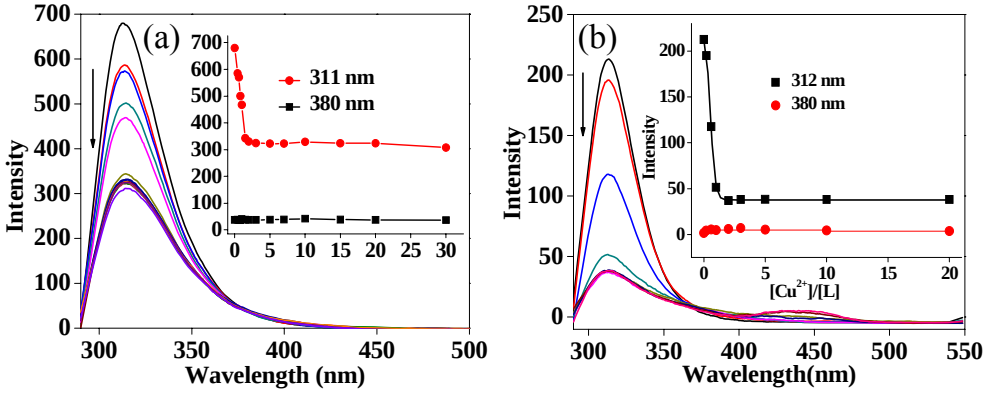


Figure S6: Fluorescence spectra obtained during the titration of **L** with Cu^{2+} in different solvent systems; (a) tetrahydrofuran; (b) acetonitrile; λ_{ex} = 280 nm. Inset of both shows relative fluorescence intensity (I/I_0) as a function of [Cu^{2+}]/[**L**] mole ratio.

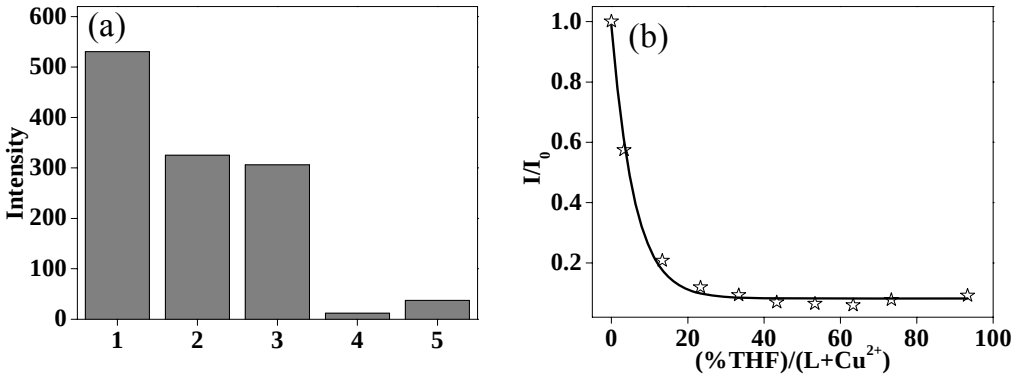


Figure S7: The effect of solvent polarity on the excimer band of 380 nm (a) Histogram showing the fluorescence intensity observed in the titration of **L** with Cu^{2+} in different solvent systems: (1) methanol, (2) aqueous-buffer-medium, (3) ethanol, (4) acetonitrile and (5) tetrahydrofuran; (b) relative fluorescence intensity (I/I_0) as a function of [% of THF]/[L+Cu^{2+}] mole ratio {[**L**] = 10 μM, [Cu^{2+}] = 30 μM; λ_{ex} = 280 nm}.

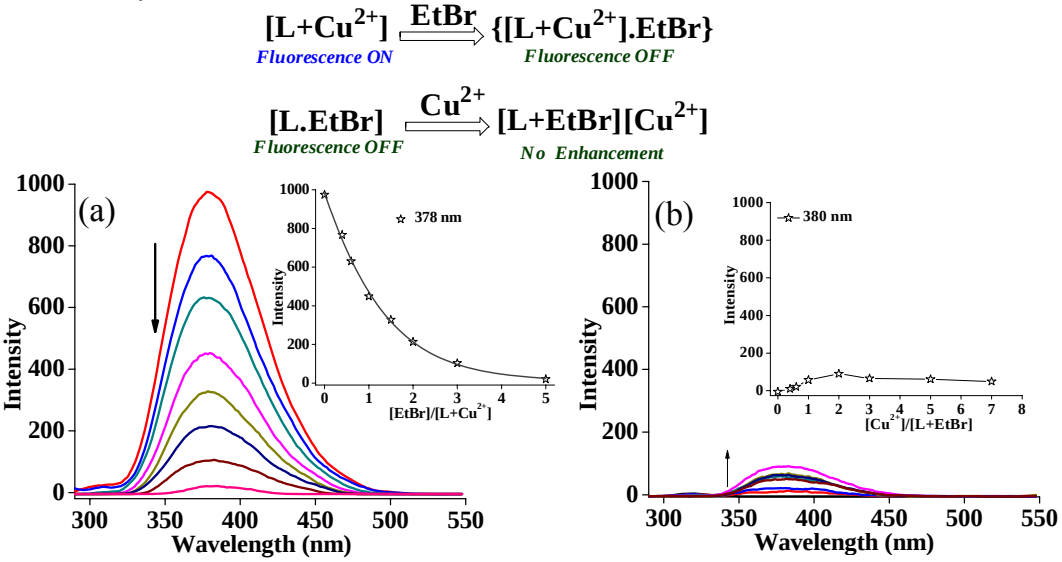


Figure S8: Fluorescence titrations with ethidium bromide (EtBr): (a) spectra obtained during the titration of {[**L**+Cu^{2+}] + EtBr}, inset shows the fluorescence intensity (I) as a function of [EtBr]/[[**L**+Cu^{2+}] mole ratio. (b) spectra obtained during the titration of {[**L**+ EtBr] + Cu^{2+}}, inset shows the fluorescence intensity (I) as a function of [Cu^{2+}]/[**L**+ EtBr] mole ratio in methanol. λ_{ex} = 280 nm. [**L**] = 10μM.

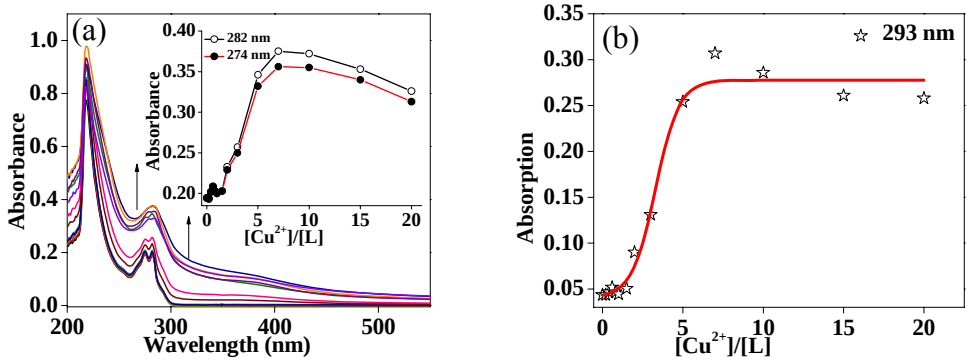


Figure S9: (a) Absorption spectra obtained during the titration **L** with Cu^{2+} in aqueous-buffer medium; inset shows the plot of absorbance *vs*. [Cu^{2+}]/ [**L**] for 274 and 282 nm absorption bands; (b) plot of absorbance *vs*. [Cu^{2+}]/ [**L**] for 293 nm absorption band.

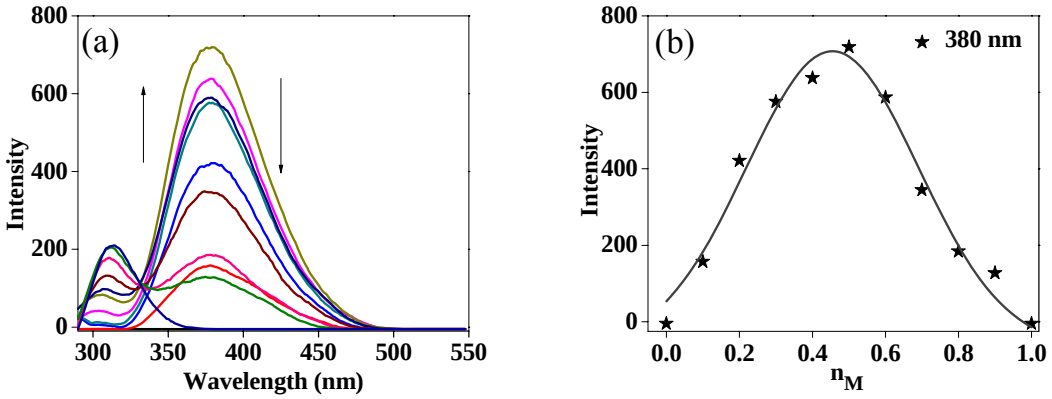


Figure S10: Job's plot for the **L** with Cu^{2+} for 1:2 ligand to metal binding. Concentration for **L** was 6 x 10^{-4} M whereas the concentration for Cu^{2+} was 12 x 10^{-4} M; (a) fluorescence intensity plot; (b) plot of fluorescence intensity as a function of the mole fraction of the metal ion.

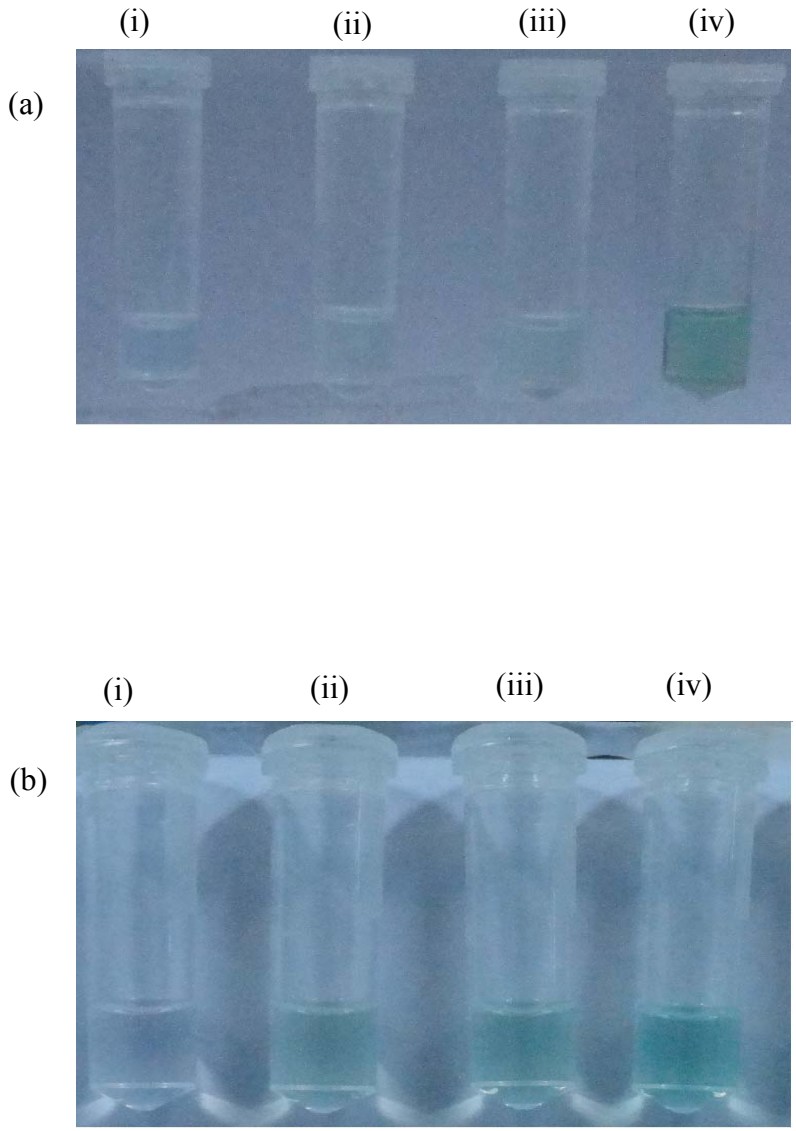


Figure S11: Visual colour change observed for the interaction of **L** with Cu^{2+} during the EPR titrations: (a) observed colour change when **L** was titrated with varying amount of Cu^{2+} (in first set of EPR samples) (i) 0, (ii) 0.25, (iii) 0.5, and (iv) 1.0 equiv. of Cu^{2+}.; (b) observed colour change when Cu^{2+} was titrated with varying amount of **L** (second set of EPR samples) (i) 0, (ii) 0.25, (iii) 0.5, and (iv) 1.0 equiv. of **L**.

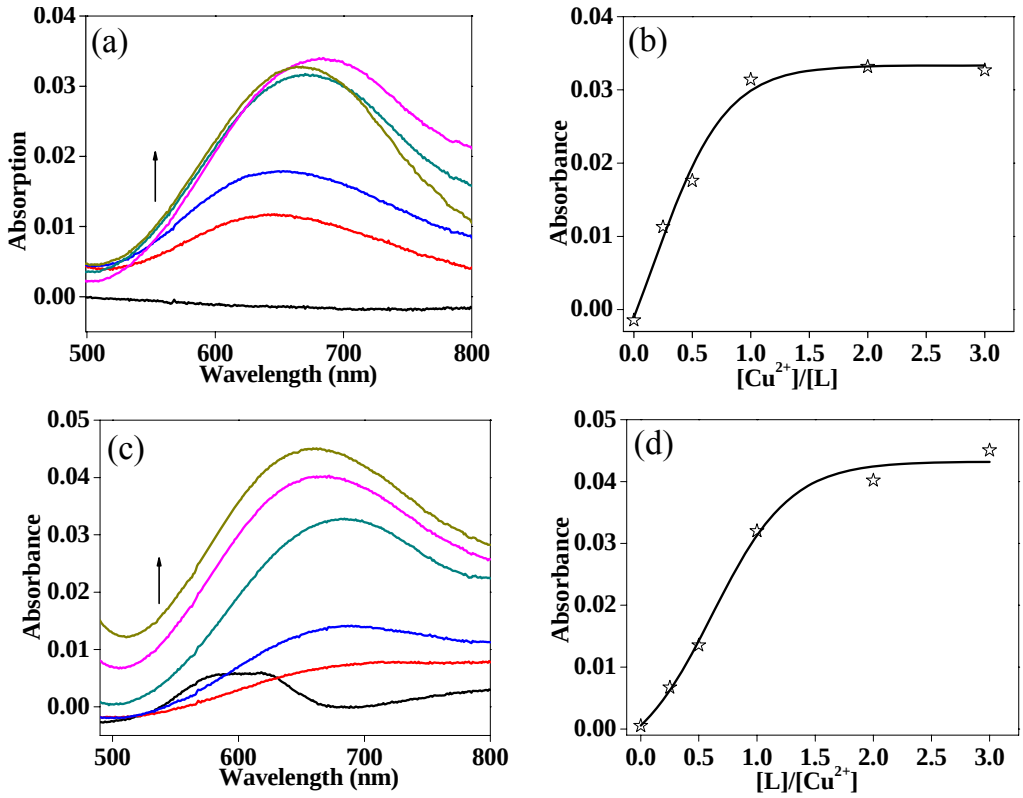


Figure S12: Absorption spectral measurements made with the samples that were used for EPR: (a) spectral traces obtained in the d→d transition region 500 – 800 nm when **L** was titrated with varying amounts of Cu^{2+}. (b) Plot of absorbance vs. $[Cu^{2+}]/[\mathbf{L}]$ for the d→d band observed at 665 nm. (c) Spectral traces observed in the d→d transition region 500 – 800 nm when Cu^{2+} was titrated with varying amount of **L**. (d) Plot of absorbance vs. $[\mathbf{L}]/[Cu^{2+}]$ for the d→d band at 665 nm.

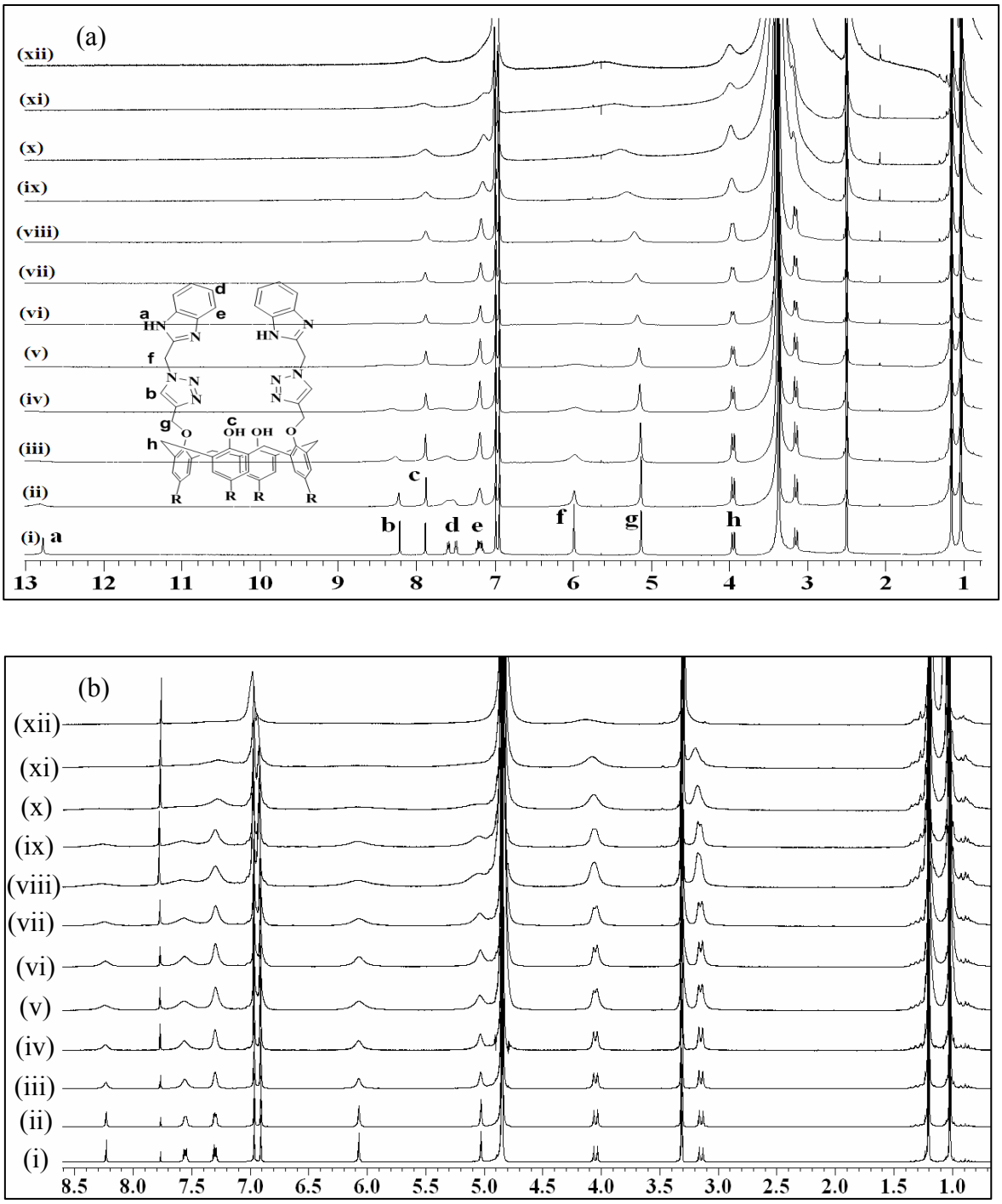


Figure S13: ^{1}H NMR spectra measured during the titration of **L** with different mole ratio of Cu^{2+} in (a) DMSO-d_6 and (b) CD_3OD (minimum amount of $CDCl_3$; [Cu]/[**L**] ratios are, (i) 0; (ii) 0.0125; (iii) 0.025; (iv) 0.0375; (v) 0.05; (vi) 0.0625; (vii) 0.075; (viii) 0.1; (ix) 0.125; (x) 0.187; (xi) 0.25; (xii) 0.5; a = benzimidazole-NH; b = triazole-H, c = phenolic-OH, d,e = benzimidaole Ar-H, f,g,h = bridged CH_2 protons. R = *tert* butyl. Spectra obtained at >0.5 equivalents of Cu^{2+} were not shown because of complete broadening of the NMR signals

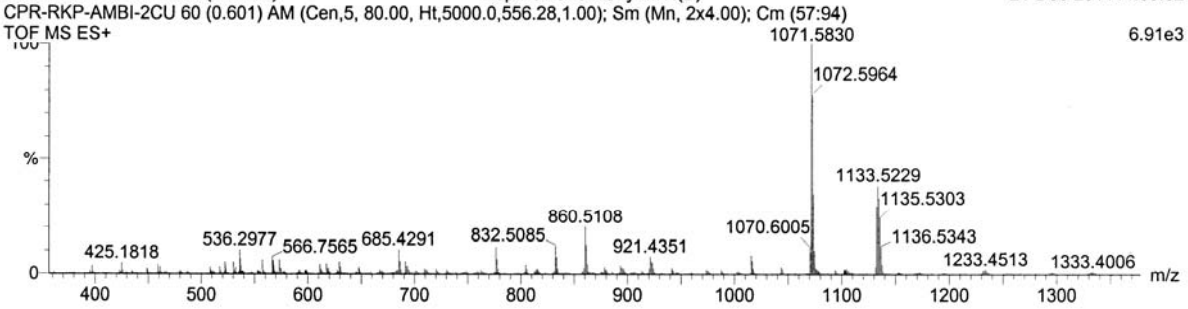
(a)

Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
88 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) 21-Dec-201114:59:52
CPR-RKP-AMBI-2CU 60 (0.601) AM (Cen,5, 80.00, Ht,5000.0,556.28,1.00); Sm (Mn, 2x4.00); Cm (57:94)
TOF MS ES+ 6.91e3



Minimum:				-1.5		
Maximum:		200.0	10.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
1133.5229	1133.5191	3.8	3.4	35.0	1	C66 H74 N10 O4 Cu

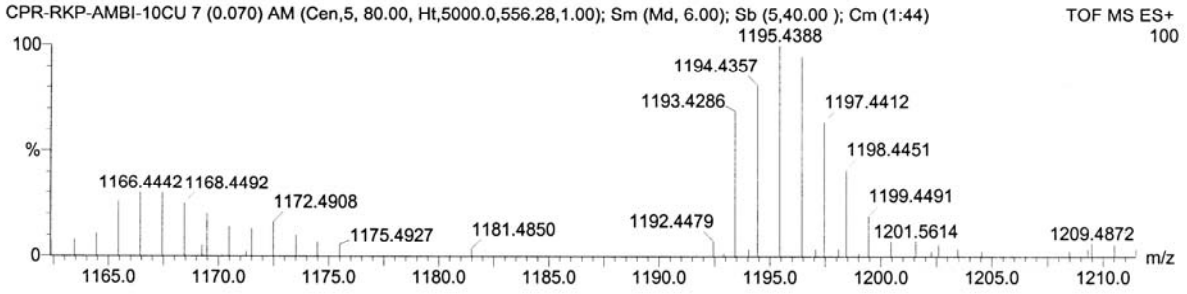
(b)

Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

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

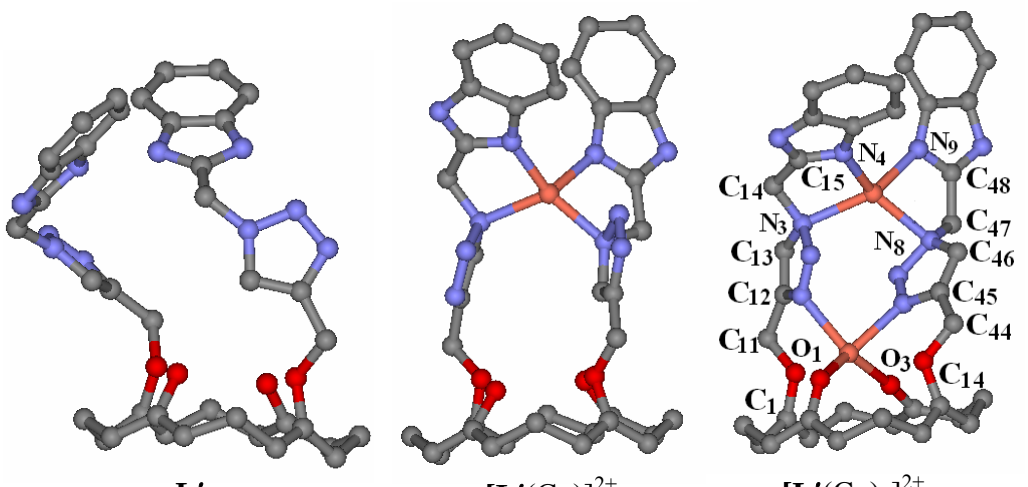
Micromass : Q-Tof micro (YA-105) Dept. Of Chemistry I.I.T.(B) 21-Dec-201115:32:53
C66H72Cu2N10O4
CPR-RKP-AMBI-10CU 7 (0.070) AM (Cen,5, 80.00, Ht,5000.0,556.28,1.00); Sm (Md, 6.00); Sb (5,40.00); Cm (1:44) TOF MS ES+ 100



Minimum:				-1.5		
Maximum:		200.0	10.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
1194.4357	1194.4330	2.7	2.3	36.0	1	C66 H72 N10 O4 Cu2

Figure S14: High resolution mass spectra of **L** with Cu^{2+}: (a) 1:1 [**L**:Cu]; (b) 1:2 [**L** : 2Cu].

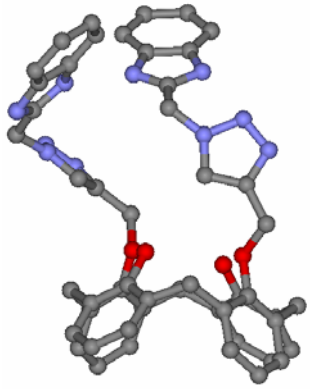
Table S4. Conformational angles (°) of the arms obtained upon optimization of **L′**, and its Cu^{2+} complexes, *viz.*, $[\mathbf{L'}(Cu)]^{2+}$ and $[\mathbf{L'}(Cu)_2]^{2+}$.



L′ $[\mathbf{L'}(Cu)]^{2+}$ $[\mathbf{L'}(Cu)_2]^{2+}$

Atoms	Dihedral Angle (°)		
	L′ (Optimized structure)	$[\mathbf{L'}(Cu)]^{2+}$	$[\mathbf{L'}(Cu)_2]^{2+}$
C1-O1-C11-C12	107.051	175.5	175.245
O1-C11-C12-C13	36.219	126.7	151.761
C11-C12-C13-N3	179.584	-173.9	177.626
C12-C13-N3-C14	174.759	-118.8	-124.232
C13-N3-C14-C15	58.726	-168.0	-176.945
N3-C14-C15-N4	-140.387	28.8	35.116
C34-O3-C44-C45	-160.145	161.1	130.912
O3-C44-C45-C46	39.964	-15.7	-177.228
C44-C45-C46-N8	178.275	-178.3	177.745
C45-C46-N8-C47	-176.712	119.3	-135.683
C46-N8-C47-C48	-125.059	172.7	-97.336
N8-C47-C48-N9	147.948	-18.5	-31.624

Table S5. Cartesian coordinates for B3LYP/6-31G optimized structure of **L′**.



Z	Coordinates			Z	Coordinates		
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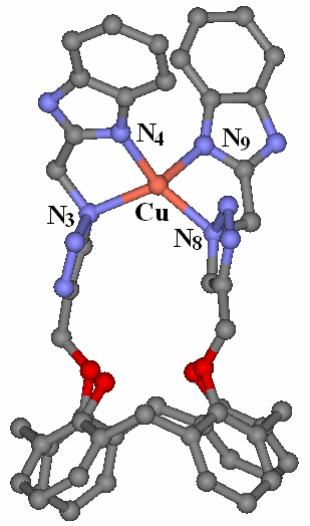
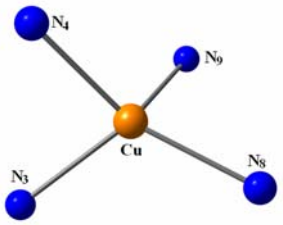
8	-1.1035	-1.50808	-0.10167	6	-1.86298	-2.63616	0.206585
8	-2.40034	0.215426	-2.45123	6	-1.99552	-3.10882	1.532095
8	-2.62885	1.801918	-0.324	6	-2.67012	-4.32152	1.741565
7	2.063504	1.191194	3.409936	1	-2.76442	-4.69894	2.755934
7	3.125503	0.423458	3.609164	6	-3.19955	-5.05316	0.676722
7	2.978245	-0.68389	2.785044	6	-3.09695	-4.54534	-0.62028
7	4.843426	-3.38785	1.215311	1	-3.5237	-5.09948	-1.45156
7	5.038708	-1.20319	0.637119	6	-2.45498	-3.3245	-0.87314
7	0.535846	1.548755	-4.05497	6	-2.48079	-2.71866	-2.27318
7	1.770036	1.525152	-3.5672	1	-2.49212	-3.53186	-3.00919
7	1.773942	0.589743	-2.53563	1	-1.57709	-2.13344	-2.43622
7	4.336753	1.488793	-0.06121	6	-3.6602	-0.44012	-2.53301
7	3.580419	2.768437	-1.75093	6	-3.71844	-1.84341	-2.48947
6	-2.18058	0.129788	2.674852	6	-4.99139	-2.43079	-2.58313
6	-3.07712	1.17715	2.956988	1	-5.07609	-3.5121	-2.557
6	-4.12738	0.895861	3.848544	6	-6.14532	-1.64962	-2.68064
1	-4.82888	1.687416	4.09294	6	-6.05374	-0.25548	-2.65977
6	-4.30411	-0.37617	4.393491	1	-6.95354	0.350848	-2.69655
6	-3.43692	-1.41146	4.036321	6	-4.8042	0.375522	-2.58278
1	-3.58917	-2.41092	4.432165	6	-1.65937	0.401564	-3.71502
6	-2.36216	-1.17768	3.168218	1	-2.06137	1.254908	-4.27105
6	-0.02114	1.276248	2.054825	1	-1.79686	-0.50346	-4.31802
1	-0.32465	1.958013	2.851285	6	-0.23548	0.636542	-3.36831
1	0.083532	1.841651	1.124586	6	0.540901	0.027286	-2.39236
6	1.241819	0.599584	2.468195	1	0.274585	-0.69699	-1.63435
6	1.820854	-0.59261	2.062951	6	3.022126	0.298881	-1.82825
1	1.49498	-1.34518	1.364991	1	3.721642	-0.15508	-2.54034
6	3.964215	-1.76456	2.870176	1	2.812776	-0.44035	-1.05523
1	3.506746	-2.66454	3.288254	6	3.630942	1.512249	-1.19057
1	4.713653	-1.39864	3.579465	6	4.768312	2.812706	0.142575
6	4.585777	-2.13053	1.562093	6	5.525909	3.365169	1.181954
6	5.513106	-3.29568	-0.01519	1	5.871635	2.746156	2.001472
6	6.013938	-4.30546	-0.84684	6	5.79787	4.731152	1.127944
1	5.917359	-5.34641	-0.56014	1	6.379822	5.191808	1.918912
6	6.632947	-3.92522	-2.0372	6	5.324619	5.535306	0.065233

1	7.032636	-4.68513	-2.70071	1	5.557124	6.595007	0.060406
6	6.75818	-2.56327	-2.39746	6	4.561876	5.000981	-0.97396
1	7.2571	-2.30557	-3.32632	1	4.196608	5.623439	-1.78319
6	6.265248	-1.54259	-1.58187	6	-4.70165	1.894861	-2.4736
1	6.385767	-0.49842	-1.85081	1	-3.73585	2.235386	-2.86262
6	5.640058	-1.92911	-0.38921	1	-5.47094	2.344634	-3.11009
6	-1.46003	-2.33093	2.733388	6	4.293745	3.629495	-0.91752
1	-0.45718	-1.95146	2.525478	6	-3.89035	2.303648	-0.06975
6	-6.12257	3.000547	-0.68683	6	-4.90067	2.412462	-1.0509
1	-6.90128	3.095317	-1.43892	1	-2.51456	1.28423	-1.16397
6	-6.34567	3.476289	0.606549	1	4.860162	-0.18463	0.618354
6	-5.33737	3.34647	1.567319	1	-1.13451	-0.77408	0.579772
1	-5.50155	3.714037	2.576524	1	3.083344	2.967712	-2.61175
6	-4.11078	2.752445	1.250387	1	-3.69388	-6.00203	0.856649
6	-3.02515	2.560306	2.301248	1	-7.11683	-2.12771	-2.7528
1	-3.15577	3.318216	3.083314	1	-7.29103	3.942758	0.862837
1	-2.05968	2.734282	1.83056	1	-5.12424	-0.56461	5.078542

Table S6. Cartesian coordinates for B3LYP/6-31G(d,p) optimized structure of **[L′(Cu)]**$^{2+}$.





Z	Coordinates			Z	Coordinates		
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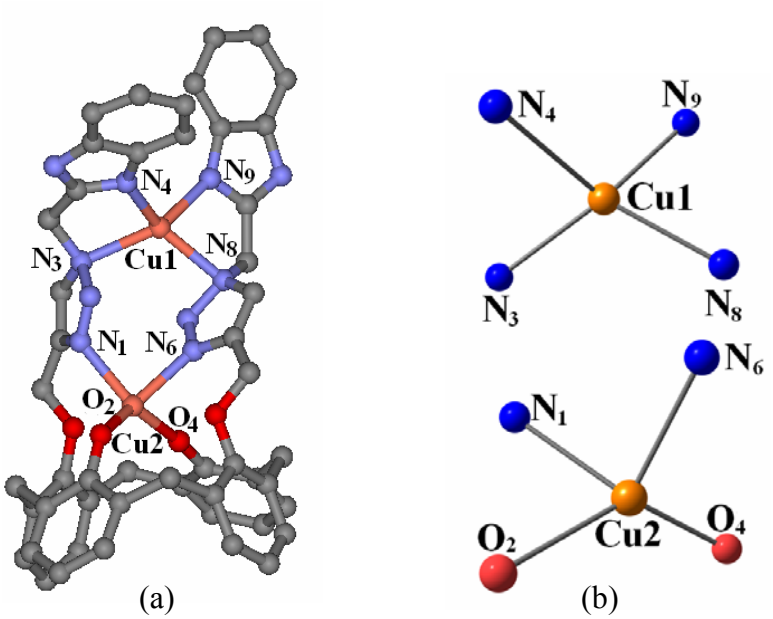
8	2.097972	0.168334	2.151544	1	3.296158	3.652022	3.126106
8	2.106159	1.591073	-0.10121	6	3.056263	2.6223	-0.1468
8	2.206941	-0.47476	-2.22912	6	3.544354	3.271086	1.032138
8	2.651959	-1.80265	0.187981	6	4.449763	4.351922	0.884671
7	-1.55278	0.248052	2.942383	1	4.826618	4.849084	1.769565
7	-2.52861	0.77853	2.05578	6	4.85101	4.799359	-0.39226
7	-1.81974	1.253015	0.853885	6	4.364756	4.153099	-1.5488
7	-4.55397	3.761119	0.242206	1	4.676341	4.494417	-2.52772
7	-4.3232	1.606656	-0.28321	6	3.473966	3.057593	-1.44238
7	-0.02657	-2.07932	-1.58086	6	3.010145	2.303054	-2.69721
7	-1.2937	-2.19495	-1.04647	1	3.013584	2.987276	-3.54444

7	-2.18909	-1.20507	-1.76344	1	1.993588	1.951803	-2.54657
7	-5.15119	-3.42276	-1.05385	6	3.515689	-0.23078	-2.73146
7	-4.44223	-1.52483	-0.11049	6	3.92124	1.105926	-3.01149
6	3.362911	0.281138	2.786497	6	5.234409	1.306042	-3.51193
6	4.108111	-0.88506	3.122714	1	5.565175	2.309228	-3.74818
6	5.377901	-0.70204	3.732149	6	6.115519	0.216433	-3.68971
1	5.959698	-1.5705	4.013474	6	5.715319	-1.09075	-3.33286
6	5.894779	0.591822	3.963617	1	6.410207	-1.91511	-3.43215
6	5.167186	1.733592	3.559388	6	4.409737	-1.33693	-2.83718
1	5.583272	2.721941	3.708508	6	1.282301	-0.74427	-3.30331
6	3.892994	1.595673	2.955308	1	1.601877	-1.59125	-3.92505
6	1.01647	0.139514	3.106336	1	1.136144	0.123029	-3.95802
1	1.169322	0.861971	3.918774	6	-0.04501	-1.09714	-2.6253
1	0.91086	-0.85196	3.564189	6	-1.32048	-0.58532	-2.78928
6	-0.27711	0.493669	2.364956	1	-1.71827	0.157726	-3.47011
6	-0.37776	1.07927	1.11401	6	-3.35726	-2.03268	-2.31292
1	0.397826	1.4284	0.425522	1	-2.97928	-2.94953	-2.7757
6	-2.23727	2.69957	0.650695	1	-3.86297	-1.43281	-3.0774
1	-1.62246	3.165873	-0.12603	6	-4.32098	-2.35059	-1.16112
1	-2.12656	3.259924	1.583886	6	-5.86097	-3.30086	0.172839
6	-3.71196	2.694949	0.212638	6	-6.83072	-4.12698	0.788268
6	-5.8166	3.346237	-0.26173	1	-7.17477	-5.04346	0.324891
6	-7.03449	4.0425	-0.44285	6	-7.31722	-3.68999	2.040184
1	-7.13608	5.088529	-0.18063	1	-8.05967	-4.28845	2.555243
6	-8.10615	3.297507	-0.9813	6	-6.85388	-2.48667	2.645524
1	-9.06192	3.783171	-1.1396	1	-7.25191	-2.19519	3.610338
6	-7.96096	1.922958	-1.32058	6	-5.88846	-1.66685	2.024197
1	-8.80964	1.388792	-1.73095	1	-5.52512	-0.75595	2.484172
6	-6.7412	1.239653	-1.13493	6	4.003118	-2.73901	-2.35599
1	-6.63368	0.194111	-1.39065	1	2.922181	-2.84702	-2.40175
6	-5.66298	1.984784	-0.59353	1	4.429287	-3.47546	-3.03316
6	3.123475	2.823812	2.442921	6	-5.40126	-2.10335	0.764367
6	4.494755	-3.05379	-0.93252	6	3.824644	-2.55967	0.228863
6	5.6556	-3.84929	-0.75983	1	3.780817	-2.95364	3.618602
1	6.169548	-4.22924	-1.63369	1	2.537781	-2.26068	2.578641
6	6.13947	-4.16506	0.526983	1	2.310465	1.026666	0.6849
6	5.470076	-3.67461	1.66884	1	2.533552	-1.49028	-0.73961
1	5.839923	-3.91939	2.656381	1	-4.31948	4.693476	0.598717
6	4.315507	-2.86852	1.535765	1	-5.22678	-4.19572	-1.72373
6	3.6062	-2.29383	2.770389	1	7.113003	0.388189	-4.07468
1	5.53434	5.634009	-0.4834	1	7.022119	-4.78184	0.636797
1	6.864098	0.709183	4.431793				

Table S7. Cartesian coordinates for B3LYP/6-31G(d,p) optimized structure of $[\mathbf{L'}_{-2H}(Cu)_2]^{2+}$.



Z	Coordinates			Z	Coordinates		
	x	y	z		x	y	z
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8	2.262104	1.430794	-0.07618	6	5.551739	-3.36676	1.799803
8	2.242497	-0.21842	-2.35002	1	5.946452	-3.56119	2.796746
8	2.491663	-2.18311	0.241368	6	4.290371	-2.78421	1.670427
6	-0.53289	0.680941	1.978013	6	3.494398	-2.33684	2.891633
6	-1.77744	1.241318	1.989639	1	3.785642	-2.9498	3.75387
7	-2.08418	1.552113	0.656876	1	2.430932	-2.48963	2.699863
7	-5.09769	3.705632	0.398276	1	4.515159	6.147364	0.069331
7	-4.72926	1.606411	-0.2522	1	7.300735	0.639241	-3.45113
6	0.002886	-0.74132	-2.69857	1	7.291877	-4.17891	0.797798
6	-1.29549	-0.55807	-3.04619	1	6.300231	1.095303	4.395603
7	-2.09355	-1.11517	-2.02146	29	-3.234409	0.105082	-0.52373
7	-4.37559	-3.83554	-1.07274	1	-4.9007	4.641811	0.722039
7	-4.23564	-1.751	-0.30018	1	-4.17148	-4.64116	-1.64635
6	2.840486	0.163209	2.937685	29	1.552645000	-0.53053	-0.16864
6	3.755398	-0.86901	3.231077	1	-1.74105	-0.07528	-3.90367
6	4.994976	-0.50336	3.770712	1	-2.47028	1.454684	2.789986
1	5.709504	-1.28554	4.011277	6	-4.98889	-2.50194	0.598444
6	5.335528	0.833069	3.969959	6	3.732351	-2.56803	0.3672
6	4.453302	1.831235	3.564325	6	4.556676	-2.84395	-0.773
1	4.747793	2.875445	3.631223	6	5.814466	-3.4259	-0.59297
6	3.202441	1.524534	3.009814	1	6.414504	-3.67123	-1.46874
6	0.395458	0.169285	3.062602	1	1.198978	0.472879	-4.0225
1	0.565369	0.953952	3.810213	7	0.035984	-1.42378	-1.47389
1	-0.06879	-0.68749	3.575462	7	-1.15336	-1.71353	-1.0896
7	-0.10403	0.671488	0.664624	6	-3.07866	-2.14317	-2.44514
7	-0.95303	1.223902	-0.1126	1	-2.55787	-2.99709	-2.89594
6	-2.6953	2.858997	0.302001	1	-3.72749	-1.69341	-3.20511
1	-2.25307	3.139428	-0.66019	6	-3.88962	-2.57591	-1.26388

1	-2.40862	3.62117	1.032821	6	-5.08725	-3.82896	0.123125
6	-4.17861	2.72339	0.168451	6	-5.78189	-4.82344	0.814043
6	-6.35087	3.17827	0.09441	1	-5.8473	-5.84218	0.445481
6	-7.63852	3.716119	0.141245	6	-6.38514	-4.44487	2.011823
1	-7.8255	4.738426	0.454125	1	-6.93259	-5.18546	2.586069
6	-8.67996	2.870954	-0.2371	6	-6.29679	-3.12319	2.497854
1	-9.69844	3.245479	-0.21766	1	-6.78104	-2.87349	3.436635
6	-8.44295	1.540509	-0.64363	6	-5.60116	-2.13739	1.803314
1	-9.28591	0.91837	-0.92718	1	-5.53059	-1.12126	2.176674
6	-7.15654	1.010395	-0.68624	6	4.050778	-2.49105	-2.16946
1	-6.96957	-0.01344	-0.99127	1	2.961381	-2.57421	-2.17227
6	-6.09907	1.848298	-0.31255	1	4.451791	-3.21818	-2.8873
6	2.377977	2.681068	2.444818	6	3.096546	2.524251	-2.58415
1	1.367192	2.346099	2.208027	1	3.257884	3.252349	-3.38915
1	2.293067	3.458048	3.216337	1	2.055708	2.191072	-2.63901
6	2.828239	2.588565	-0.05075	6	3.588352	0.004695	-2.64705
6	2.959812	3.310646	1.187171	6	4.019884	1.332988	-2.8122
6	3.56118	4.569054	1.207035	6	5.371116	1.538479	-3.11632
1	3.647528	5.101297	2.154608	1	5.732664	2.55503	-3.24936
6	4.046742	5.16786	0.036906	6	6.256016	0.463917	-3.20856
6	3.901813	4.485575	-1.17859	6	5.812168	-0.83027	-2.93839
1	4.256004	4.953044	-2.09745	1	6.521149	-1.65317	-2.93754
6	3.302324	3.227565	-1.24903	6	4.471489	-1.09039	-2.61936
1	1.604747	-1.26149	-4.02629	6	1.30514	-0.4172	-3.3852

Table S8. Percentage of MOs present on the fragments of **L′**, **[L′(Cu)]**$^{2+}$ and [**L′**$_{-2H}$ $(Cu)_2$]$^{2+}$ for different HOMO/LUMO which were generated by using Chemissian 1.77 software.

L′					
MOs	Energy eV	Cone	Triazole	Benzimidazole	Copper
HOMO – 1	-5.909	96	0	0	0
HOMO	-5.657	99	0	0	0
LUMO	-1.138	0	20	77	0
LUMO + 1	-0.886	0	67	31	0
[**L′**(Cu)]$^{2+}$					
HOMO (α) – 1	-10.276	100	0	0	0
HOMO (α)	-10.079	97	0	0	0
LUMO (α)	-7.598	0	95	0	0
LUMO (α) + 1	-7.282	0	91	0	0
HOMO (β) – 1	-9.960	96	0	0	0
HOMO (β)	9.764	43	12	13	32
LUMO (β)	-9.375	43	12	12	33
LUMO (β) + 1	-7.598	0	94	0	0
[**L′**$_{-2H}$ $(Cu)_2$]$^{2+}$					
HOMO – 1	-10.065	83	0	0	12
HOMO	-9.417	65	10	0	26
LUMO	-8.514	0	31	62	7
LUMO + 1	-7.030	0	74	16	8

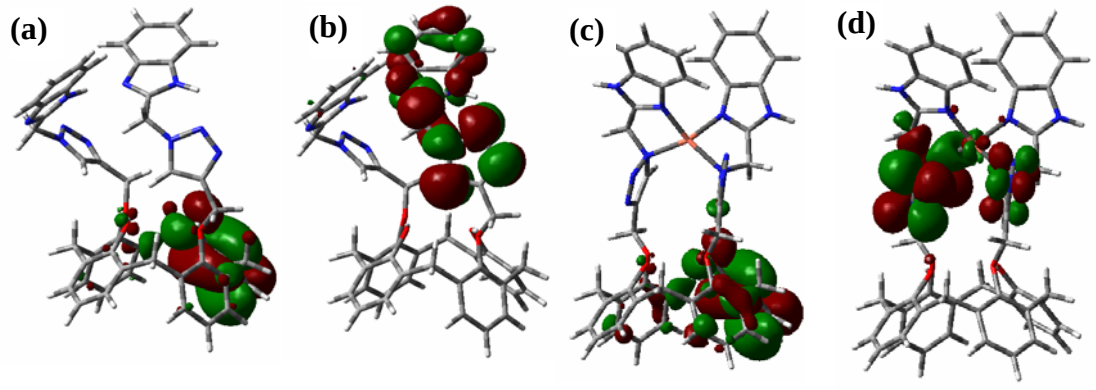

Figure S15: Pictorial representation of the molecular orbitals (MOs) present on different fragments of **L** and [**L′**(Cu)]$^{2+}$: (a) HOMO of **L′**; (b) LUMO of **L′**; (c) HOMO (α) of [**L′**(Cu)]$^{2+}$; (d) LUMO (α) of [**L′**$_{-2H}$ $(Cu)_2$]$^{2+}$.