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Structural changes in Cu(II) complexes of potential octadentate ligands by coordination with carboxylate/carboxylic acid: DFT, TD-DFT and experimental studies

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Supplementary Materials

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Table S1. Geometrical parameters (bond length in Å) of ligands and complexes

	L^1	L^2H	L^2	$[CuL^1]^{2+}$	$[CuL^2H]^{2+}$	$[CuL^2]^{+}$
Bond length						
N1-C2	1.367	1.373	1.376	1.314	1.315	1.314
C2-N3	1.323	1.316	1.319	1.375	1.376	1.378
C2-C10	1.502	1.505	1.503	1.501	1.499	1.501
C10-N41	1.476	1.450	1.467	1.480	1.487	1.476
N41-C42	1.470	1.458	1.467	1.475	1.477	1.475
C42-C43	1.532	1.545	1.533	1.525	1.522	1.529
C43-N44	1.473	1.479	1.463	1.494	1.500	1.476
N44-C45	1.464	1.472	1.462	1.499	1.500	1.480
C45-C46	1.532	1.535	1.533	1.518	1.523	1.525
C46-N47	1.473	1.475	1.470	1.497	1.491	1.494
N47-C20	1.470	1.470	1.471	1.489	1.495	1.493
C20-C12	1.506	1.507	1.504	1.491	1.491	1.491
C12-N11	1.368	1.372	1.364	1.352	1.328	1.322
C12-N13	1.318	1.319	1.323	1.328	1.345	1.352
N47-C30	1.451	1.469				
C30-C22	1.518	1.499	1.508	1.505	1.492	1.494
C22-N21	1.315	1.368	1.359	1.313	1.375	1.371
C22-N23	1.376	1.320	1.331	1.378	1.314	1.317
N41-C40	1.482	1.438	1.468	1.483	1.463	1.459
C40-C32	1.506	1.519	1.511	1.500	1.499	1.500
C32-N31	1.377	1.380	1.323	1.361	1.328	1.324
C32-N33	1.319	1.313	1.372	1.319	1.355	1.360
N44-C48	1.476	1.466	1.474	1.502	1.476	1.474
C48-C49	1.500	1.522	1.545	1.505	1.518	1.544
C49-O50	-	1.218	1.271		1.223	1.310
C49-051	-		1.258		1.323	1.219
C49-N50	1.377					
C49-N51	1.315					
C49-OH51		1.336				
C49-N50				1.378		
C49N51				1.313		
Cu-N3				2.09	2.06	2.06
Cu-N41				3.02	2.81	3.05
Cu-N44				2.28	2.23	2.43
Cu-N47				2.15	2.13	2.16
Cu-N13				2.05	2.01	2.05
Cu-050					2.64	2.27
Cu-N50				2.29		

Table S2. Geometrical parameters (bond angles in degrees) of complexes

	$[CuL^1]^{2+}$	$[CuL^2H]^{2+}$	$[CuL^2]^{+}$
Bond angle			
N3-Cu-N41	68.1	71.3	67.9
N3-Cu-N44	100.6	99.9	98.2
N3-Cu-N47	167.7	174.6	171.6
N3-Cu-N13	93.7	95.4	95.0
N3-Cu-O50		89.6	94.70
N3-Cu-N50	96.5		
N41-Cu-N44	69.80	73.9	66.5
N41-Cu-N47	102.5	113.7	104.3
N41-Cu-N13	100.5	101.1	91.2
N41-Cu-O50		134.6	134.1
N41-Cu-N50	138.0		
N44-Cu-N47	82.7	83.8	80.9
N44-Cu-N13	157.7	161.2	147.0
N44-Cu-O50		69.3	75.2
N44-Cu-N50	75.6		
N47-Cu-N13	79.8	81.7	81.6
N47-Cu-O50		88.0	93.2
N47-Cu-N50	95.7		
N13-Cu-O50		121.87	133.7
N13-Cu-N50	119.8		

Table S3. Selected bond lengths (Å) and angles for $[CuL^2]^{+}$

Cu(1)-N(13)	2.012(7)	Cu(1)-N(3)	2.035(7)
Cu(1)-N(47)	2.119(7)	Cu(1)-N(44)	2.148(7)
Cu(1)-O(50)	2.299(6)		
N(13)-Cu(1)-N(3)	94.0(3)	N(13)-Cu(1)-N(47)	80.8(3)
N(3)-Cu(1)-N(47)	174.1(3)	N(13)-Cu(1)-N(44)	158.6(3)
N(3)-Cu(1)-N(44)	102.5(3)	N(47)-Cu(1)-N(44)	83.3(3)
N(13)-Cu(1)-O(50)	120.8(3)	N(3)-Cu(1)-O(50)	89.0(3)
N(47)-Cu(1)-O(50)	91.4(3)	N(44)-Cu(1)-O(50)	73.7(2)

Table S4. Electronic absorption spectral and magnetic moment data of copper(II) compounds

Compounds	d-d bands [a]	CT bands [a]	Magnetic moments (μ_{eff})[b] BM
$CuL^1(ClO_4)_2.H_2O$	599 (430)	310 (710)	1.72
$CuL^1Cl_2.2H_2O.MeOH$	604(435)	330 (735)	1.72
$CuL^2H(ClO_4)_2.H_2O.MeOH$	675 (350)	315 (810)	1.78
$CuL^2HCl_2.2H_2O$	672(330)	315 (800)	1.79
$[CuL^2](ClO_4).(OH_2)_{4.5}$	596 (450)	312 (716)	1.76
$[CuL^2]Cl.2H_2O$	600 (465)	326 (730)	1.78

Concentration: a ≈ 1.0 x 10^{-2}; λ_{max} in nm with ε /dm^3 mol^{-1} cm^{-1} in parentheses. B) $\mu_{eff} = [\mu^2 complex /2]^{½}$

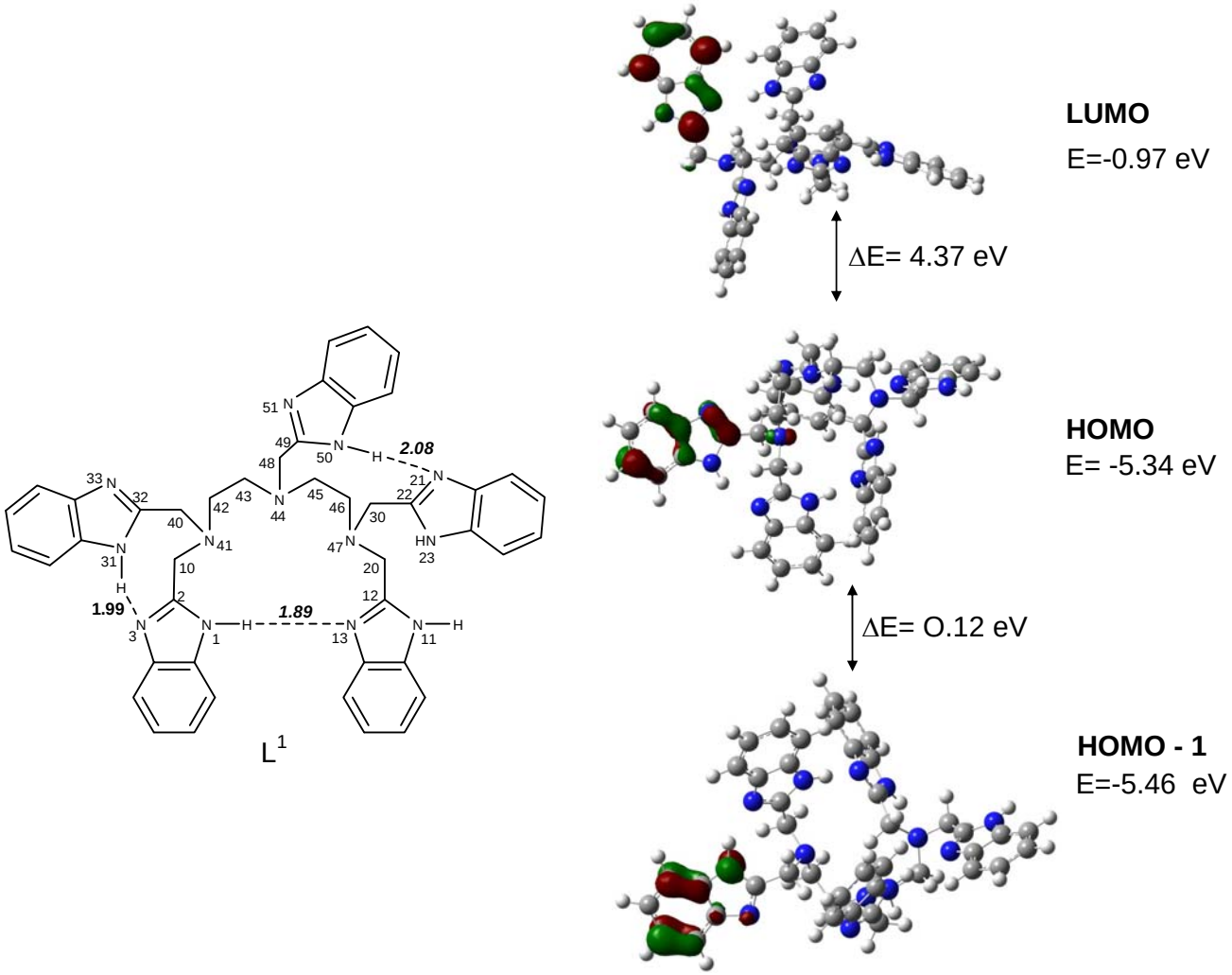


Fig. S1.Structural data and molecular orbital analysis of L^1 (*MO orbitals, green = bonding; red: antibonding).*

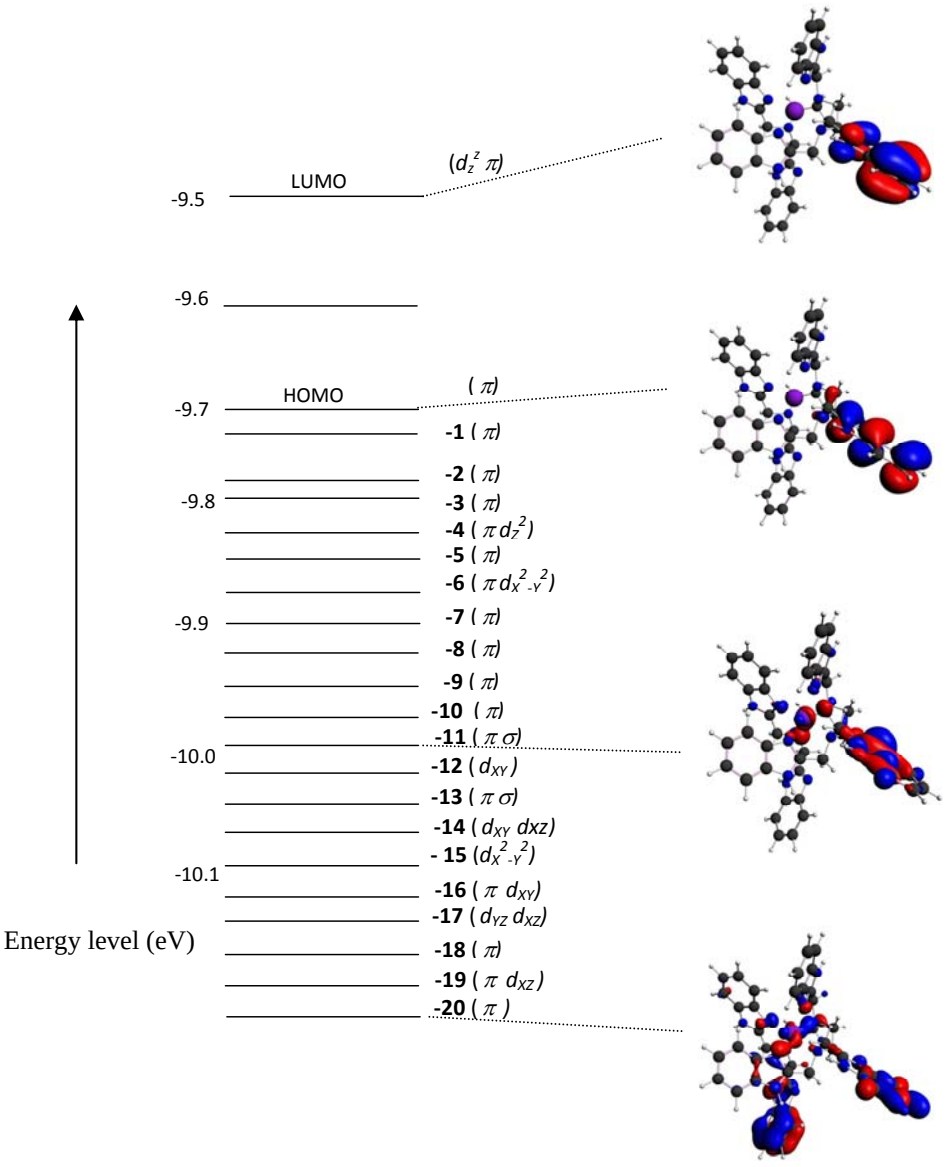


Fig. S2. Frontier molecular orbital energy level diagram of $[CuL^1]^{2+}$

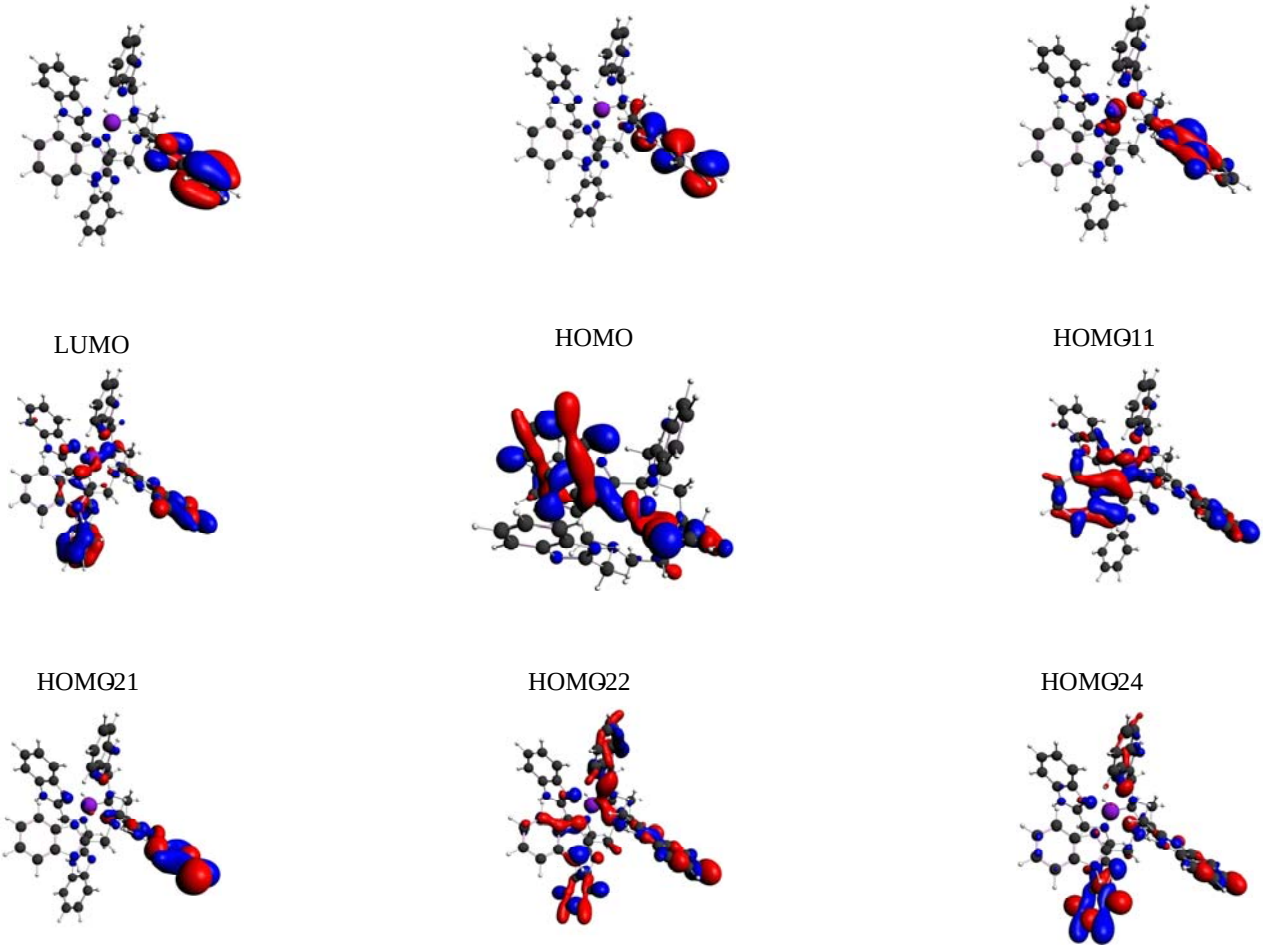


Fig.S3. HOMO-LUMO studies of $[CuL^{1}]^{2+}$

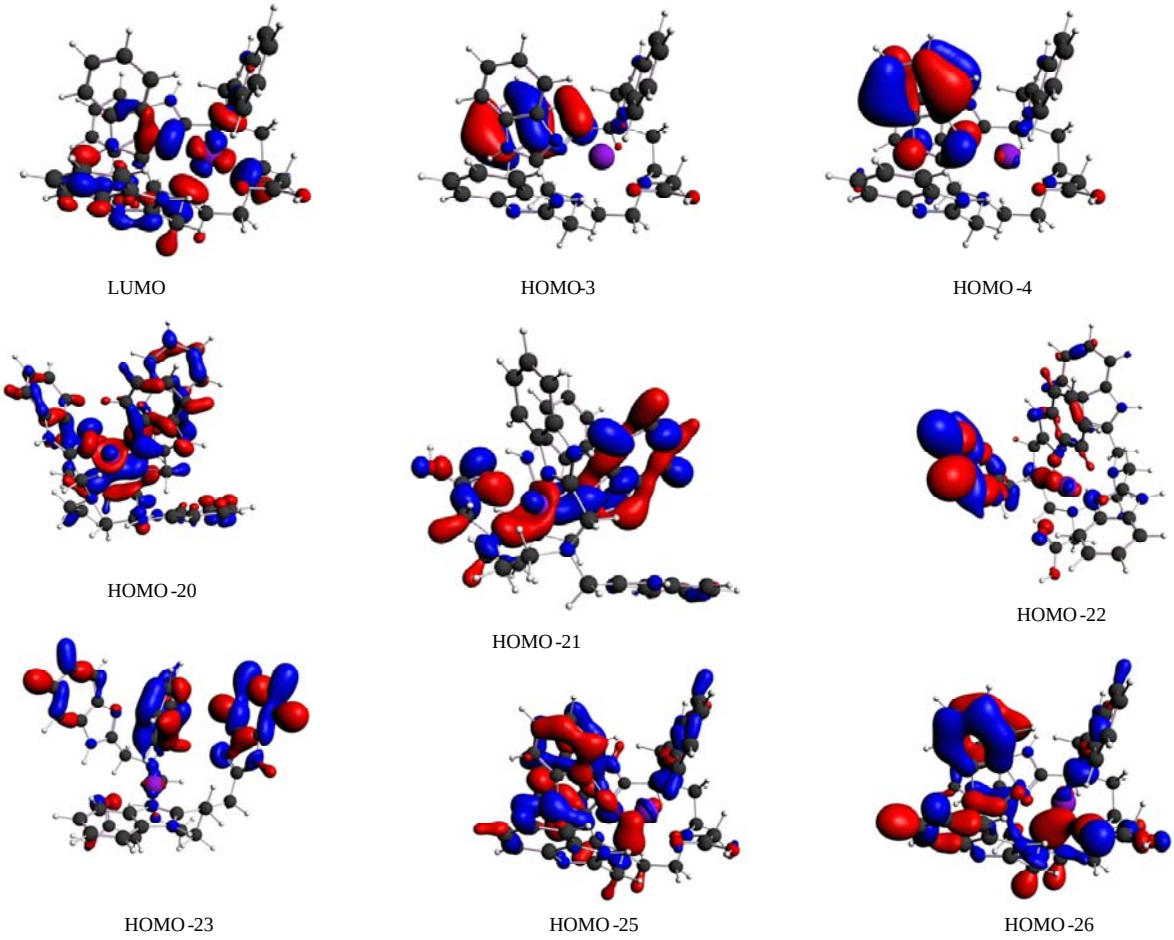


Fig.S4. HOMO-LUMO studies of $[CuL^{1}H]^{2+}$

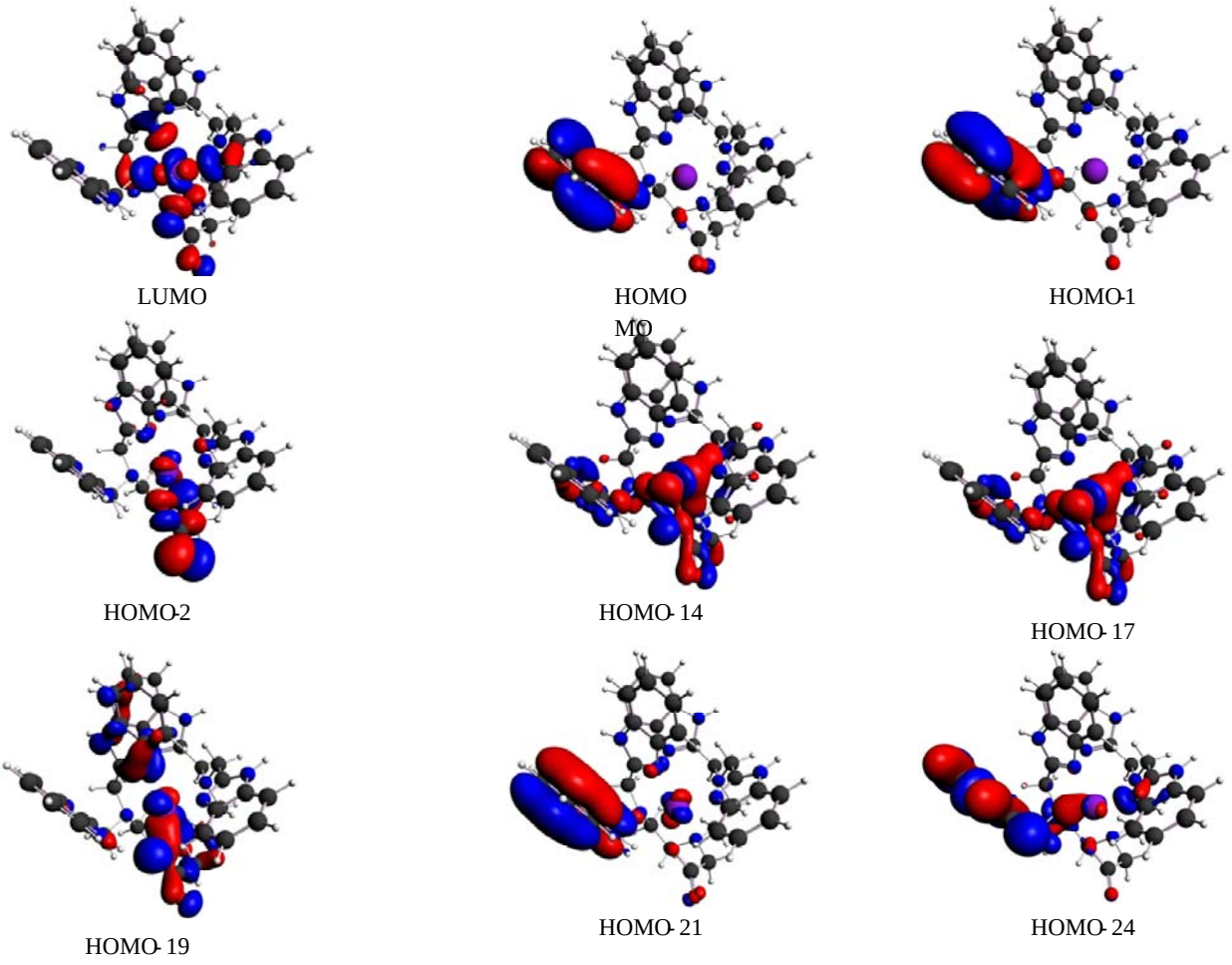
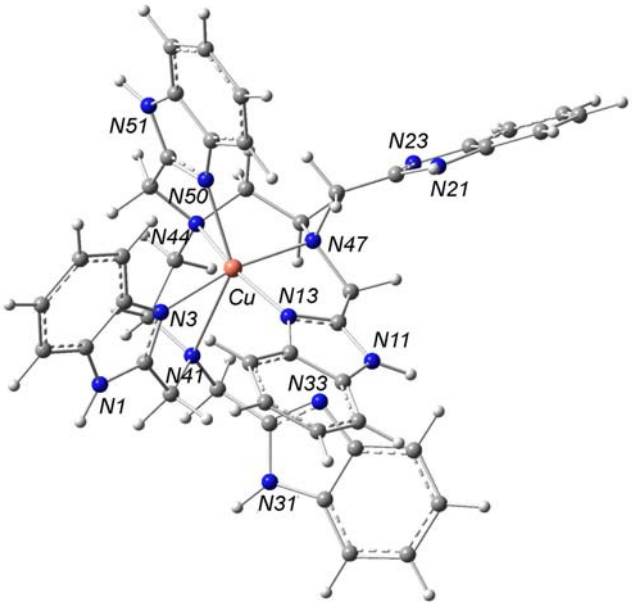
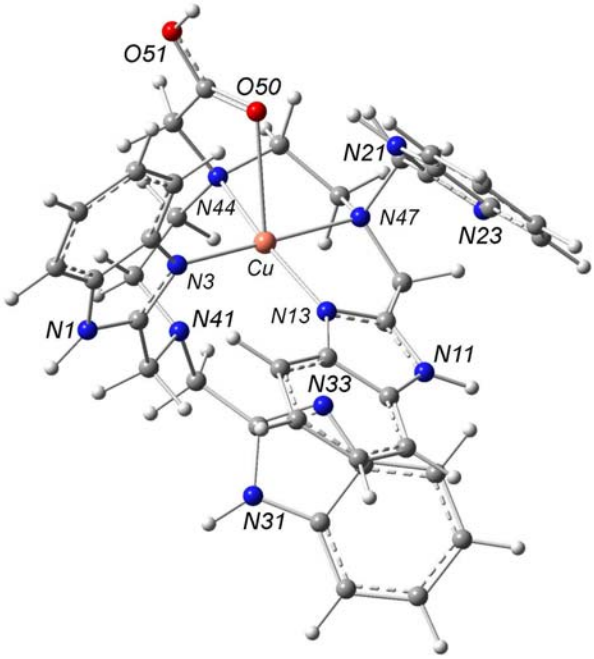


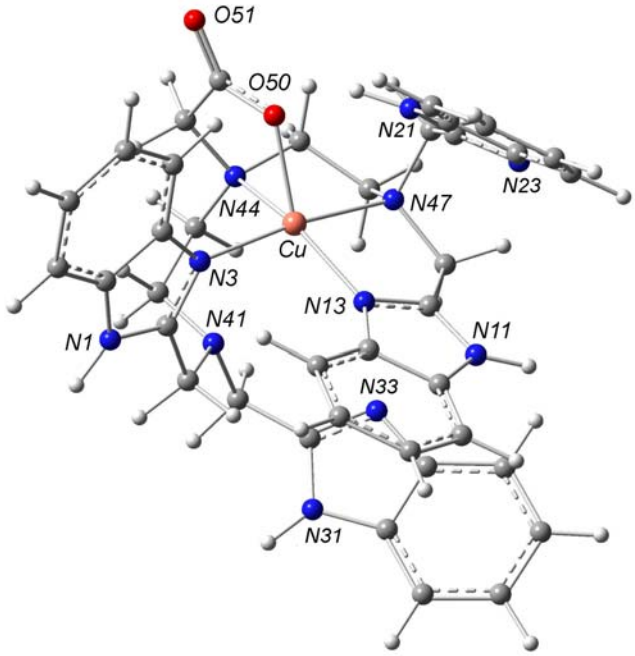
Fig.S5. HOMO-LUMO studies of $[CuL^2]^+$



$[CuL^1]^{2+}$



$[CuL^2H]^{2+}$



$[Cu\ L^2]^{+}$

Fig. S6. Optimized structures of the copper complexes