Electronic Supplementary Information

Designing of antiferromagnetically coupled mono-, di- and tri- bridged copper(II) based catecholase models by varying "Auxiliary Part" of ligand and anionic co-ligand

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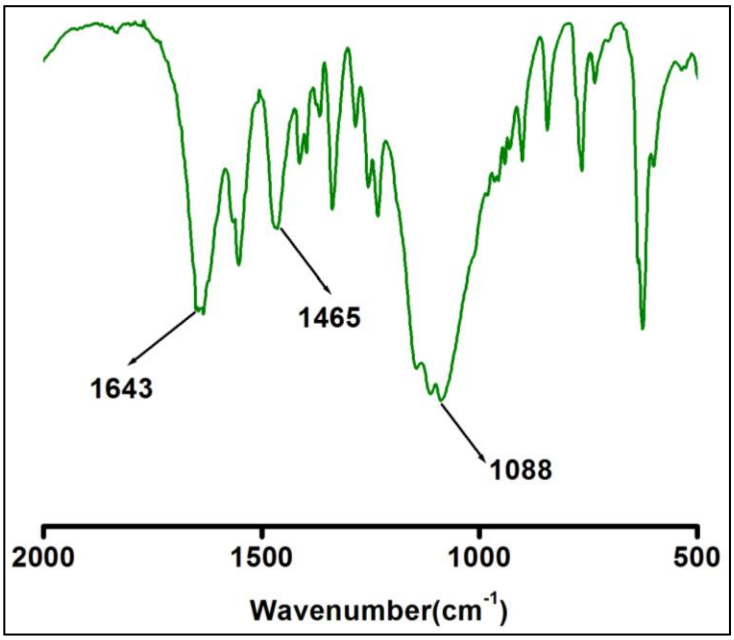

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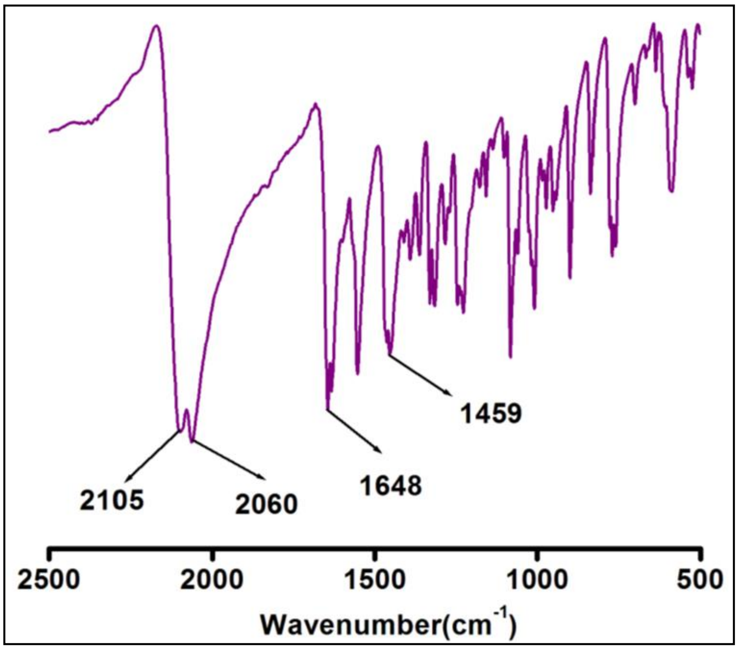
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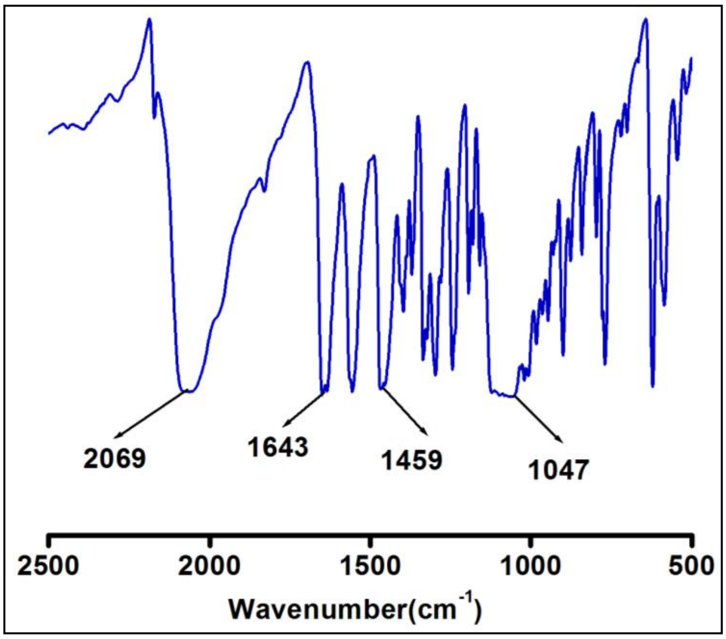
(b)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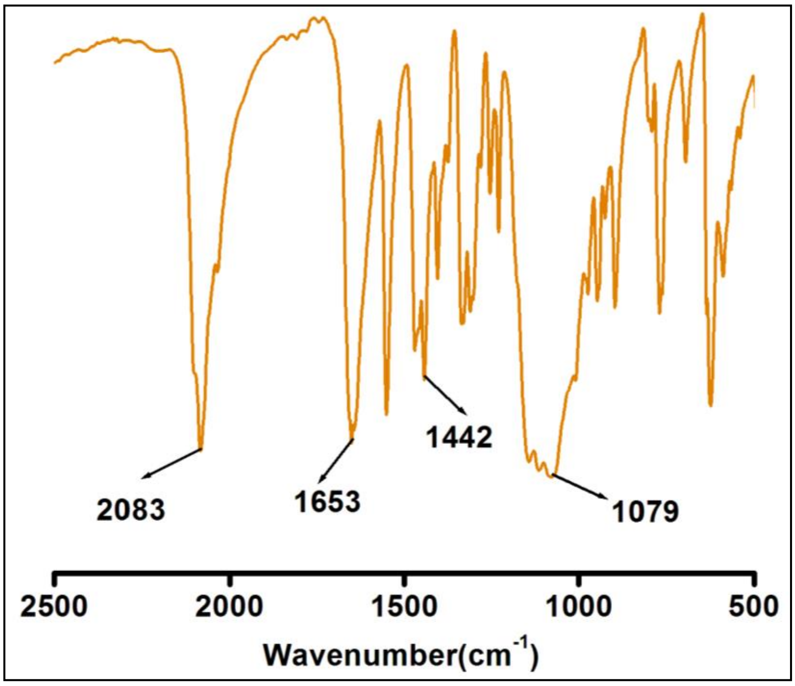
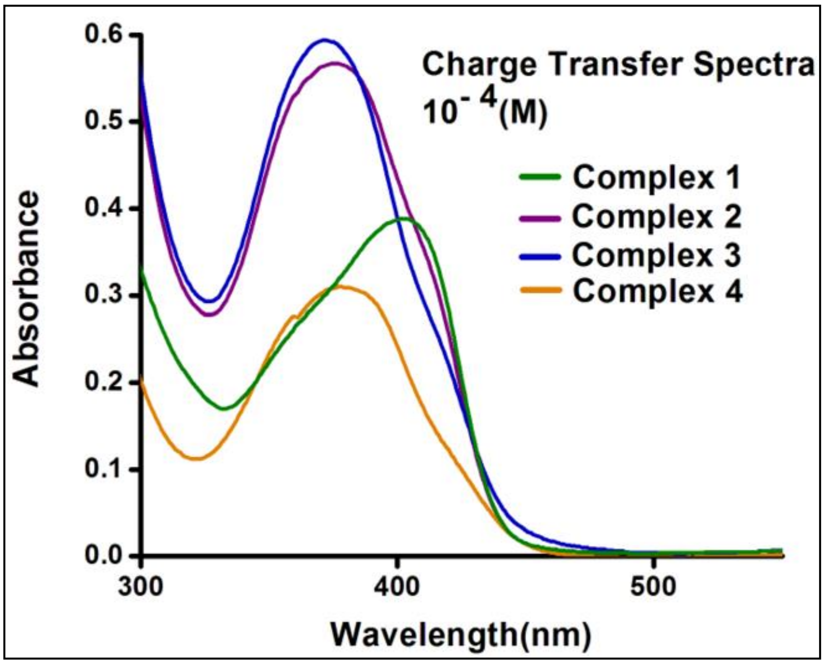
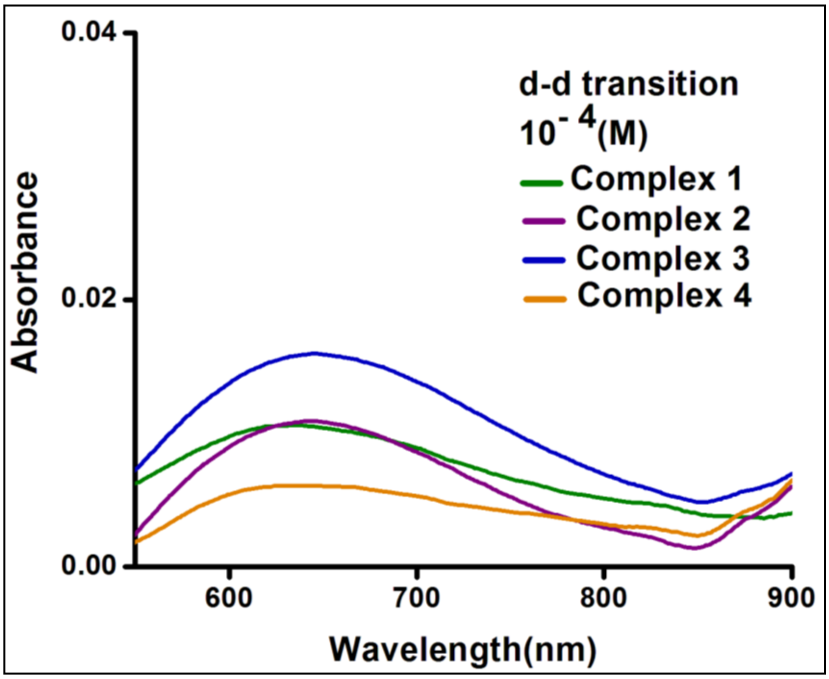


(d)

Fig. S1 FT-IR spectrum of (a) complex **1**, (b) complex **2**, (c) complex **3** and (d) complex **4**.



(a)



(b)

Fig. S2 (a) Charge transfer Spectra and (b) d-d transition of complexes in DMSO medium.

Table S1. Selected bond lengths (Å) and angles (°) for Complex **1**

Cu(1)-O(1)	1.967(3)	Cu(2)-O(1)	1.947(3)
Cu(1)-N(1)	1.920(4)	Cu(2)-N(3)	1.906(4)
Cu(1)-N(2)	2.018(4)	Cu(2)-N(4)	2.017(4)
Cu(1)-O(2)	1.885(3)	Cu(2)-O(2)	1.886(3)
Cu(1)-O(1w)	2.549(4)	Cu(2)-O(10)	2.584(4)
Cu(1)-O(7)	2.827(4)	Cu(1)-Cu(2)	2.9634(9)
O(2)-Cu(1)-N(1)	168.68(14)	O(2)-Cu(2)-O(1)	79.05(13)
O(2)-Cu(1)-O(1)	78.58(12)	N(3)-Cu(2)-O(1)	91.34(14)
N(1)-Cu(1)-O(1)	90.68(13)	O(2)-Cu(2)-N(4)	102.83(15)
O(2)-Cu(1)-N(2)	103.61(15)	N(3)-Cu(2)-N(4)	86.75(16)
N(1)-Cu(1)-N(2)	86.78(16)	O(1)-Cu(2)-N(4)	178.02(14)
O(1)-Cu(1)-N(2)	174.62(14)	Cu(2)-O(1)-Cu(1)	98.42(12)
O(2)-Cu(2)-N(3)	170.25(15)	Cu(1)-O(2)-Cu(2)	103.61(14)

Table S2. Selected bond lengths (Å) and angles (°) for Complex **4**

Cu(1)-O(1)	1.967(4)	Cu(2)-O(1)	1.954(4)
Cu(1)-N(1)	1.927(5)	Cu(2)-N(3)	1.931(5)
Cu(1)-N(2)	2.014(5)	Cu(2)-N(4)	2.006(5)
Cu(1)-N(5)	1.932(5)	Cu(2)-N(5)	1.953(5)
Cu(1)-O(2)	2.564(5)	Cu(2)-O(3)	2.460(5)
Cu(1)-O(7)	2.726(5)	Cu(1)-Cu(2)	2.9746(13)

N(1)-Cu(1)-N(5)	169.4(2)	N(3)-Cu(2)-O(1)	91.33(18)
N(1)-Cu(1)-O(1)	91.44(19)	N(5)-Cu(2)-O(1)	80.46(19)
N(5)-Cu(1)-O(1)	80.63(19)	N(3)-Cu(2)-N(4)	86.2(2)
N(1)-Cu(1)-N(2)	86.2(2)	N(5)-Cu(2)-N(4)	101.9(2)
N(5)-Cu(1)-N(2)	102.1(2)	O(1)-Cu(2)-N(4)	177.49(19)
O(1)-Cu(1)-N(2)	176.2(2)	Cu(1)-O(1)-Cu(2)	98.68(17)
N(3)-Cu(2)-N(5)	167.7(2)	Cu(1)-N(5)-Cu(2)	99.9(2)

Table S3. Selected bond lengths (Å) and angles (°) for Complex **2**

Cu(1)-O(1)	1.981(3)	Cu(2)-O(1)	1.977(3)
Cu(1)-N(1)	1.953(4)	Cu(2)-N(3)	1.944(4)
Cu(1)-N(2)	2.038(5)	Cu(2)-N(4)	2.057(5)
Cu(1)-N(5)	1.934(6)	Cu(2)-N(7)	1.919(5)
Cu(1)-N(6)	2.252(5)	Cu(2)-S(2) '	2.6634(16)
		Cu(1)-Cu(2)	3.3628(2)
N(5)-Cu(1)-N(1)	176.3(2)	N(7)-Cu(2)-N(3)	175.5(2)
N(5)-Cu(1)-O(1)	91.09(18)	N(7)-Cu(2)-O(1)	91.84(16)
N(1)-Cu(1)-O(1)	87.59(15)	N(3)-Cu(2)-O(1)	87.46(16)
N(5)-Cu(1)-N(2)	95.9(2)	N(7)-Cu(2)-N(4)	95.2(2)
N(1)-Cu(1)-N(2)	84.4(2)	N(3)-Cu(2)-N(4)	84.12(19)
O(1)-Cu(1)-N(2)	162.4(2)	O(1)-Cu(2)-N(4)	161.27(19)
N(5)-Cu(1)-N(6)	93.8(2)	N(7)-Cu(2)-S(2) '	88.95(16)
N(1)-Cu(1)-N(6)	89.9(2)	N(3)-Cu(2)-S(2) '	95.48(14)
O(1)-Cu(1)-N(6)	97.1(2)	O(1)-Cu(2)-S(2) '	92.37(11)
N(2)-Cu(1)-N(6)	98.5(2)	N(4)-Cu(2)-S(2) '	105.05(17)
		Cu(2)-O(1)-Cu(1)	116.36(15)

S(2)' at -x+1/2,-y+1/2,z+1/2.

Table S4. Selected bond lengths (Å) and angles (°) for Complex **3**

Cu-N(1)	1.924(4)	Cu-O(1)	1.978(3)
Cu-N(2)	2.041(5)	Cu-O(2)	2.652(5)
Cu-N(3)	1.907(4)	Cu-Cu'	3.225(1)
N(3)-Cu-N(1)	171.4(2)	O(1)-Cu-N(2)	163.73(15)
N(3)-Cu-O(1)	91.10(16)	O(1)-Cu-O(2)	97.70(14)
N(1)-Cu-O(1)	89.02(15)	O(2)-Cu-N(1)	86.82(18)
N(3)-Cu-N(2)	97.54(19)	O(2)-Cu-N(2)	96.85(19)
N(1)-Cu-N(2)	84.49(19)	O(2)-Cu-N(3)	84.6(2)
		Cu’-O(1)-Cu	109.2(2)

Symmetry codes (') -x,y,-z+3/2.

Table S5. Relative Gibbs free enegies in methanol solution for compounds involved in the reaction shown in the Schemes 1 and 2 (for optimization in gas phase, relative Gibbs free enegies after solvent effects appear in parenthesis). All energies are in kcal/mol.

Compds	X in L^X					
	*t*Bu		Me		Cl	
$[Cu_2(\kappa^5\text{-L})(\mu\text{-OH})]^{2+}$ ($\mathbf{A}^{E}$)	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)
$[Cu_2(\kappa^5\text{-L})(\mu\text{-OH})(ClO_4)]^{+}$ ($\mathbf{A}^{X}$)	+7.6	(+8.7)	+8.2	(+8.7)	+5.9	(+8.3)
$[Cu_2(\kappa^5\text{-L})(\mu\text{-OH})(ClO_4)_2]$ ($\mathbf{A}^{Y}$)	+15.1	(+15.7)	+15.5	(+15.3)	+13.5	(+15.1)
$[Cu_2(\kappa^5\text{-L})(\mu\text{-OH})(ClO_4)(H_2O)]^{+}$($\mathbf{A}^{W}$)	+8.8	(+17.1)	+9.5	(+17.0)	+7.6	(+16.4)
$[Cu_2(\kappa^5\text{-L})(\mu\text{-}N_3)]^{2+}$ ($\mathbf{B}^{E}$)	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)
$[Cu_2(\kappa^5\text{-L})(\mu\text{-}N_3)(ClO_4)]^{+}$ ($\mathbf{B}^{X}$)	+6.7	(+7.3)	+8.9	(+7.0)	+7.6	(+6.8)
$[Cu_2(\kappa^5\text{-L})(\mu\text{-}N_3)(ClO_4)_2]$ ($\mathbf{B}^{Y}$)	+14.9	(+15.0)	+17.4	(+14.7)	+15.2	(+14.0)
$[Cu_2(\kappa^5\text{-L})(\mu\text{-}N_3)(ClO_4)(H_2O)]^{+}$ ($\mathbf{B}^{W}$)	+11.8	(+16.5)	+11.3	(+16.0)	+8.2	(+15.5)
$[Cu_2(\kappa^5\text{-L})(\mu\text{-NCS})]^{2+}$ ($\mathbf{C}^{E}$)	+8.3	(+11.7)	+8.0	(+11.5)	+8.9	(+11.8)
$[Cu_2(\kappa^5\text{-L})(\mu\text{-NCS})]^{2+}$ ($\mathbf{C}^{E}$)	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)
$[Cu_2(\kappa^5\text{-L})(NCS)_2]^{+}$ ($\mathbf{C}^{N}$)	-1.3	(-6.4)	-0.8	(-6.8)	-1.4	(-7.3)
$[Cu_2(\kappa^5\text{-L})(NCS)_2(ClO_4)_2]^{-}$ ($\mathbf{D}^{Cl}$)	+18.3	(+13.4)	+17.5	(+13.0)	+14.4	(+12.1)
$[Cu_2(\kappa^5\text{-L})(NCS)_2(\kappa N\text{-NCS})_2]^{-}$ ($\mathbf{D}^{N}$)	+19.8	(-0.3)	+19.0	(-1.3)	+18.4	(-2.1)
$[Cu_2(\kappa^5\text{-L})(NCS)_2(\kappa S\text{-SCN})_2]^{-}$ ($\mathbf{D}^{S}$)	+15.8	(+2.2)	+15.2	(+1.9)	+14.4	(+0.8)

Table S6. Main geometric parameters for the optimized molecular structures in methanol solution (optimizations in gas phase are shown in parenthesis). Distances in angstroms, angles in degrees.

Compounds	*t*Bu		Me		Cl	
$[Cu_2(\kappa^5\text{-L})(\mu\text{-OH})]^{2+}$ ($\mathbf{A}^{E}$)						
Cu···Cu	3.01	(3.06)	3.01	(3.06)	3.01	(3.06)
$Cu\text{-}O_{Ar}$	2.00	(1.99)	2.00	(2.00)	2.01	(2.00)
Cu-OH	1.98	(1.94)	1.98	(1.94)	1.98	(1.94)
$Cu\text{-}N_{Im}$	1.97	(1.95)	1.97	(1.95)	1.98	(1.95)
$Cu\text{-}N_{Am}$	2.08	(2.07)	2.08	(2.06)	2.08	(2.06)
θ	178	(180)	175	(180)	171	(180)
$[Cu_2(\kappa^5\text{-L})(\mu\text{-OH})(ClO_4)]^{+}$ ($\mathbf{A}^{X}$)						
Cu···Cu	3.01	(2.97)	3.01	(2.97)	3.01	(2.97)
$Cu\text{-}O_{Ar}$	2.00	(2.00)	2.01	(2.01)	2.01	(2.01)
Cu-OH	1.99	(1.96)	1.98	(1.96)	1.98	(1.96)
$Cu\text{-}N_{Im}$	1.98	(1.97)	1.98	(1.97)	1.98	(1.97)
$Cu\text{-}N_{Am}$	2.09	(2.09)	2.08	(2.09)	2.08	(2.08)

Cu⋯O_{Cl}	3.27 3.31	(2.37) (2.39)	3.27 3.33	(2.37) (2.38)	3.32 3.32	(2.36) (2.37)
O(H)⋯O_{Cl}	3.11	(2.92)	3.09	(2.92)	3.10	(2.92)
θ	179	(161)	179	(161)	179	(160)
$[Cu_2(\kappa^5\text{-L})(\mu\text{-OH})(ClO_4)_2]$ (**A**^{Y})						
Cu⋯Cu	3.01	(2.94)	3.01	(2.94)	3.01	(2.94)
Cu-O_{Ar}	2.01	(1.99)	2.00	(1.99)	2.01	(1.99)
Cu-OH	1.98	(1.96)	1.98	(1.96)	1.98	(1.96)
Cu-N_{Im}	1.98	(1.98)	1.98	(1.98)	1.98	(1.98)
Cu-N_{Am}	2.09	(2.08)	2.09	(2.08)	2.08	(2.08)
Cu⋯O_{Cl}	3.99 4.45	(2.72) (2.79)	3.59 3.64	(2.71) (2.79)	3.34 3.76	(2.69) (2.76)
O(H)⋯O_{Cl}	3.07	(2.89)	3.05	(2.89)	3.07	(2.88)
Cu⋯O_{Cl}	3.23 3.27	(2.45) (2.50)	3.25 3.26	(2.44) (2.49)	3.23 3.27	(2.44) (2.48)
θ	180	(174)	180	(174)	179	(174)
$[Cu_2(\kappa^5\text{-L})(\mu\text{-OH})(ClO_4)(H_2O)]^+$ (**A**^{W})						
Cu⋯Cu	3.04	(2.99)	3.04	(2.99)	3.04	(3.00)
Cu-O_{Ar}	2.01	(2.00)	2.02	(2.00)	2.02	(2.01)
Cu-OH	2.00	(1.98)	1.99	(1.98)	1.99	(1.98)
Cu-N_{Im}	1.98	(1.97)	1.98	(1.97)	1.98	(1.97)
Cu-N_{Am}	2.09	(2.08)	2.09	(2.08)	2.08	(2.08)
Cu⋯O_{Cl}	3.34 3.54	(2.37) (2.41)	3.33 3.52	(2.37) (2.41)	3.32 3.50	(2.36) (2.40)
O(H)⋯O_{Cl}	3.03	(2.86)	3.03	(2.86)	3.02	(2.86)
O_{OH}⋯(H)O_W	3.04	(2.78)	2.74	(2.78)	2.74	(2.78)
θ	178	(163)	177	(163)	177	(162)
$[Cu_2(\kappa^5\text{-L})(\mu\text{-N}_3)]^{2+}$ (**B**^{E})						
Cu⋯Cu	3.12	(3.11)	3.12	(3.11)	3.12	(3.11)
Cu-O_{Ar}	2.02	(2.01)	2.02	(2.01)	2.02	(2.02)
Cu-N_3	2.05	(2.00)	2.05	(2.00)	2.05	(2.00)
Cu-N_{Im}	1.97	(1.95)	1.97	(1.95)	1.97	(1.95)
Cu-N_{Am}	2.08	(2.08)	2.08	(2.08)	2.08	(2.08)
θ	176	(177)	177	(177)	177	(177)
$[Cu_2(\kappa^5\text{-L})(\mu\text{-N}_3)(ClO_4)]^+$ (**B**^{X})						
Cu⋯Cu	3.13	(3.04)	3.12	(3.04)	3.12	(3.04)
Cu-O_{Ar}	2.03	(2.03)	2.03	(2.03)	2.03	(2.03)
Cu-N_3	2.05	(2.02)	2.04	(2.02)	2.05	(2.02)

Cu-N$_{Im}$	1.96	(1.97)	1.97	(1.97)	1.97	(1.97)
Cu-N$_{Am}$	2.09	(2.09)	2.09	(2.09)	2.08	(2.09)
Cu···O$_{Cl}$	3.18 3.27	(2.30) (2.30)	3.16 3.20	(2.29) (2.29)	3.20 3.40	(2.29) (2.29)
θ	172º	(154)	179º	(154)	175º	(154)
[Cu$_2$(κ^5-L)(μ-N$_3$)(ClO$_4$)$_2$] (**B**^{Y})						
Cu···Cu	3.12	(3.03)	3.12	(3.03)	3.11	(3.03)
Cu-O$_{Ar}$	2.02	(2.01)	2.03	(2.01)	2.03	(2.02)
Cu-N$_3$	2.05	(2.01)	2.05	(2.01)	2.04	(2.01)
Cu-N$_{Im}$	1.97	(1.98)	1.97	(1.98)	1.97	(1.98)
Cu-N$_{Am}$	2.09	(2.10)	2.09	(2.10)	2.08	(2.10)
Cu···O$_{Cl}$	3.23 3.39	(2.48) (2.49)	3.25 3.35	(2.47) (2.49)	3.40 3.42	(2.47) (2.48)
Cu···O$_{Cl}$	3.17 3.27	(2.50) (2.52)	3.16 3.28	(2.50) (2.52)	3.20 3.22	(2.49) (2.50)
θ	178º	(180)	180º	(180)	180º	(180)
[Cu$_2$(κ^5-L)(μ-N$_3$)(ClO$_4$)(H$_2$O)]$^+$ (**B**^{W})						
Cu···Cu	3.11	(3.05)	3.11	(3.05)	3.11	(3.05)
Cu-O$_{Ar}$	2.02	(2.04)	2.02	(2.04)	2.03	(2.05)
Cu-N$_3$	2.05	(2.01)	2.05	(2.01)	2.05	(2.01)
Cu-N$_{Im}$	1.97	(1.97)	1.97	(1.97)	1.97	(1.97)
Cu-N$_{Am}$	2.08	(2.10)	2.08	(2.10)	2.08	(2.10)
Cu···O$_{Cl}$	3.24 3.34	(2.28) (2.40)	3.25 3.34	(2.27) (2.41)	3.20 3.26	(2.27) (2.41)
Cu···O$_{W}$	3.28	(2.70)	3.22	(2.70)	3.28	(2.68)
θ	176	(156)	176	(156)	176	(156)
[Cu$_2$(κ^5-L)(μ-NCS)]$^{2+}$ (**C**^{E})						
Cu···Cu	3.10	(3.08)	3.07	(3.08)	3.07	(3.07)
Cu-O$_{Ar}$	2.01	(2.00)	2.00	(2.00)	2.01	(2.01)
Cu-NCS	2.10	(2.03)	2.10	(2.03)	2.09	(2.02)
Cu-N$_{Im}$	1.97	(1.96)	1.97	(1.96)	1.97	(1.96)
Cu-N$_{Am}$	2.08	(2.08)	2.08	(2.08)	2.08	(2.08)
θ	172	(173)	166	(174)	166	(174)
[Cu$_2$(κ^5-L)(NCS)$_2$]$^+$ (**C**^{N})						
Cu···Cu	3.39	(3.33)	3.40	(3.33)	3.41	(3.33)
Cu-O$_{Ar}$	2.05	(2.02)	2.05	(2.02)	2.05	(2.02)
Cu-N$_{E\text{-}NCS}$	1.97	(1.92)	1.97	(1.92)	1.97	(1.92)
Cu-N$_{Im}$	1.98	(1.97)	1.98	(1.97)	1.98	(1.97)

Cu-N_{Am}	2.12	(2.11)	2.12	(2.11)	2.12	(2.10)
χ	30.3	(32.5)	30.8	(32.6)	30.9	(32.6)
$[Cu_2(\kappa^5\text{-L})(NCS)_2(ClO_4)_2]^-$ (**D**^{Cl})						
Cu···Cu	3.43	(3.47)	3.43	(3.47)	3.43	(3.46)
Cu-O_{Ar}	2.06	(2.02)	2.06	(2.02)	2.07	(2.02)
Cu-$N_{E\text{-}NCS}$	1.97	(1.94)	1.97	(1.94)	1.97	(1.94)
Cu-N_{Im}	1.98	(1.98)	1.98	(1.98)	1.98	(1.98)
Cu-N_{Am}	2.12	(2.12)	2.12	(2.12)	2.12	(2.12)
Cu···O_{Cl}	3.22 3.22	(2.53) (2.53)	3.21 3.21	(2.52) (2.52)	3.21 3.22	(2.50) (2.50)
χ	31.3	(41.2)	31.4	(41.1)	31.4	(41.5)
$[Cu_2(\kappa^5\text{-L})(NCS)_2(\kappa N\text{-}NCS)_2]^-$ (**D**^{N})						
Cu···Cu	3.70	(3.62)	3.57	(3.62)	3.58	(3.62)
Cu-O_{Ar}	2.10	(2.05)	2.08	(2.05)	2.09	(2.05)
Cu-$N_{E\text{-}NCS}$	1.98	(1.96)	1.99	(1.96)	1.98	(1.96)
Cu-N_{Im}	1.98	(2.01)	2.00	(2.01)	2.00	(2.02)
Cu-N_{Am}	2.13	(2.16)	2.14	(2.16)	2.13	(2.16)
Cu-$N_{A\text{-}NCS}$	2.40	(2.22)	2.42	(2.21)	2.42	(2.21)
χ	42.0	(46.9)	39.0	(46.8)	39.1	(46.9)
$[Cu_2(\kappa^5\text{-L})(NCS)_2(\kappa S\text{-}SCN)_2]^-$ (**D**^{S})						
Cu···Cu	3.47	(3.65)	3.43	(3.65)	3.44	(3.69)
Cu-O_{Ar}	2.06	(2.07)	2.06	(2.07)	2.07	(2.08)
Cu-$N_{E\text{-}NCS}$	1.96	(1.94)	1.97	(1.94)	1.97	(1.94)
Cu-N_{Im}	1.98	(1.99)	1.98	(1.99)	1.98	(1.99)
Cu-N_{Am}	2.15	(2.18)	2.12	(2.18)	2.12	(2.18)
Cu···$S_{A\text{-}NCS}$	3.55	(2.69)	4.59	(2.68)	4.58	(2.65)
χ	32.3	(45.8)	31.3	(45.8)	31.3	(46.6)

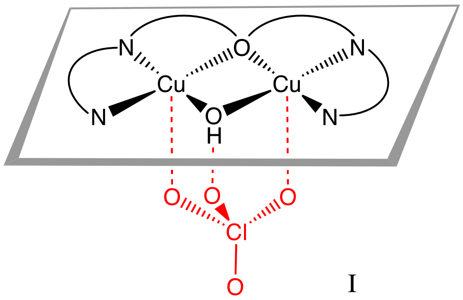
Atomic names: O_{Ar}, N_{Im} and N_{Am} are donor atoms from the phenolic oxigens, iminic and aminic nitrogens of the ligand; OH (or O_{OH} especificating a lone pair on the oxigen) and N_3 represent the donor atom in the bridging ligand in edge-sharing unit; N_{Im} and N_{Am} are donor atoms from the phenolic oxigens, iminic and aminic nitrogens of the ligand; O_{Cl} and O_W are the oxigen atoms of perchlorate and water; $N_{E\text{-}NCS}$ is the nitrogen of equatorial thiocyanate; and, N/$S_{A\text{-}NCS}$ represent the corresponding donor of apical thiocyanate.

Angular parameters: θ is defined as the bent angle between CuO_2 (or CuON) planes in the Cu_2O_2 (or Cu_2ON) ring; χ is defined as the tilt angle between Cu plane and chelate ligand.

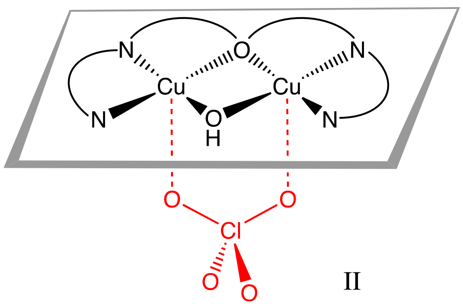
Table S7. Strutural motifs of perchlorate anion bound to edge-sharing binuclear copper(II) having phenoxo and hydroxo bridges and four terminal nitrogen donors.

a) Perchlorate anion is bound to both copper atoms into binuclear unit

Refcode	Type	$Cu_A\cdots O_{Cl}$	$Cu_B\cdots O_{Cl}$	$O_H\cdots O_{Cl}$
IQOLAB ‡	**I**	2.554	3.324	3.041
ZOJSOG *	**I**	3.139	3.197	2.948
PEVBOI $,‡	**I**	3.736	3.822	2.959
DOYGON	**II**	2.450	2.586	
PEVBOI $	**II**	2.464	2.610	
LAJTIZ §	**II**	2.467	3.222	
SICDUD $	**II**	2.481	2.597	
OBOWOS $,§	**II**	2.499	2.528	
FAMJUY *	**II**	2.506	2.788	
HAGLAF §	**II**	2.526	2.603	
GUQKOS ‡	**II**	2.534	2.587	
GIRQAZ	**II**	2.536	2.923	
ZOJSOG *	**II**	2.543	2.661	
KENYOR $,‡	**II**	2.561	2.999	
SEKVEK *	**II**	2.568	2.621	
GIRQAZ	**II**	2.579	2.832	
FAXDIR *	**II**	2.613	2.653	
VERMAI *	**II**	2.645	2.805	
SEKVEK *	**II**	2.657	2.664	
CANTET *	**II**	2.685	2.822	
FAMJUY *	**II**	2.692	3.066	
CANTET *	**II**	2.720	3.070	
FAXDIR *	**II**	2.773	2.940	
POVVUR $,§	**II**	2.859	3.118	
VERMAI *	**II**	2.939	3.033	



I



II

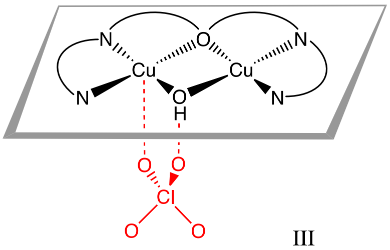
* Two perchlorates are coordinated to the same binuclear unit as a bridging ligand;
$ Two perchlorates are non-equivalent bound; § Some copper atom is coordinated by water (or alcohol) molecule; ‡ An important disorder in

found for the perchlorate anion.

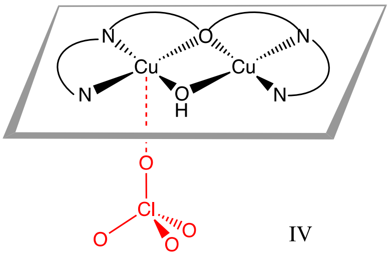
b) Perchlorate anion is bound to only one copper atom into binuclear unit

Refcode	Type	Cu···O$_{Cl}$	O$_H$···O$_{Cl}$
DADJAT §	**III**	2.543	2.898
LAJTIZ §	**III**	3.619	2.958
IQOLAB ‡	**IV**	2.402	
SIRLEK §,‡	**IV**	2.528	
KENYOR $	**IV**	2.598	
POVVUR $,§,‡	**IV**	2.627	
SICDUD $	**IV**	2.716	
OBOWOS $,§	**IV**	2.838	
SAVMEH §	**IV**	2.990	
DIJBAA §	**IV**	3.212	
DADJAT §	**IV**	3.256	
GETYOT	**IV**	3.455	
GETYOT	**IV**	3.731	
COSKAW	**V**	3.532	
CEKRIV §	**VI**	2.388	
POKDID	**VI**	2.449 2.673	
UZUXET §,‡	**VI**	2.536 2.682	
DUDFUD §	**VI**	2.644 2.712	
GIRQAZ	**VI**	2.723	
GIRQAZ	**VI**	2.730	

$ Two perchlorates are non-equivalent bound; § Some copper atom is coordinated by water (or alcohol) molecule; ‡ An important disorder in found for the perchlorate anion.



III



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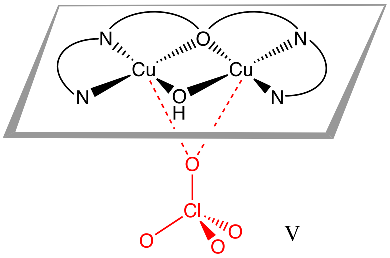
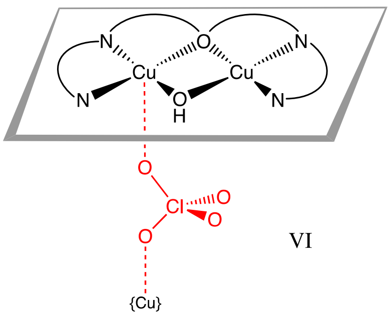


V



VI

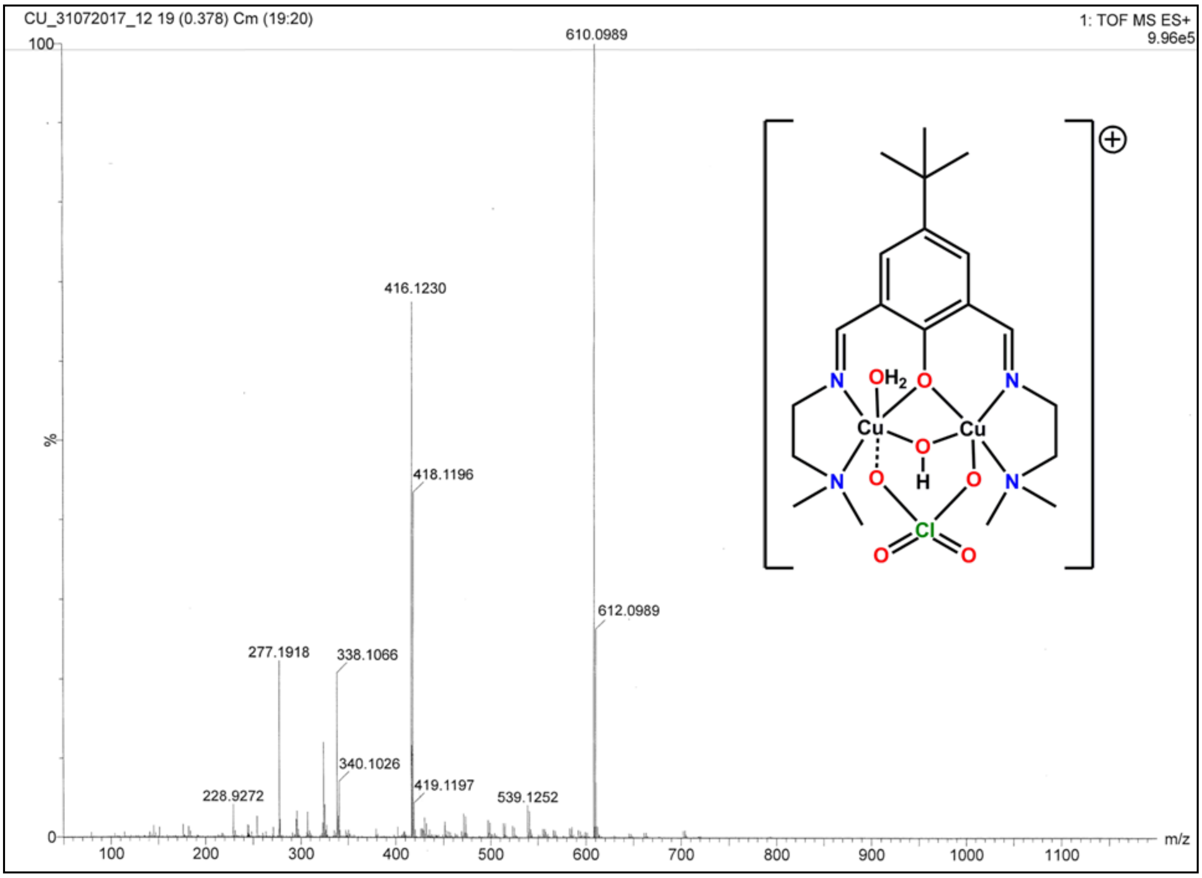


Fig. S3 ESI-MS spectrum of complex **1**

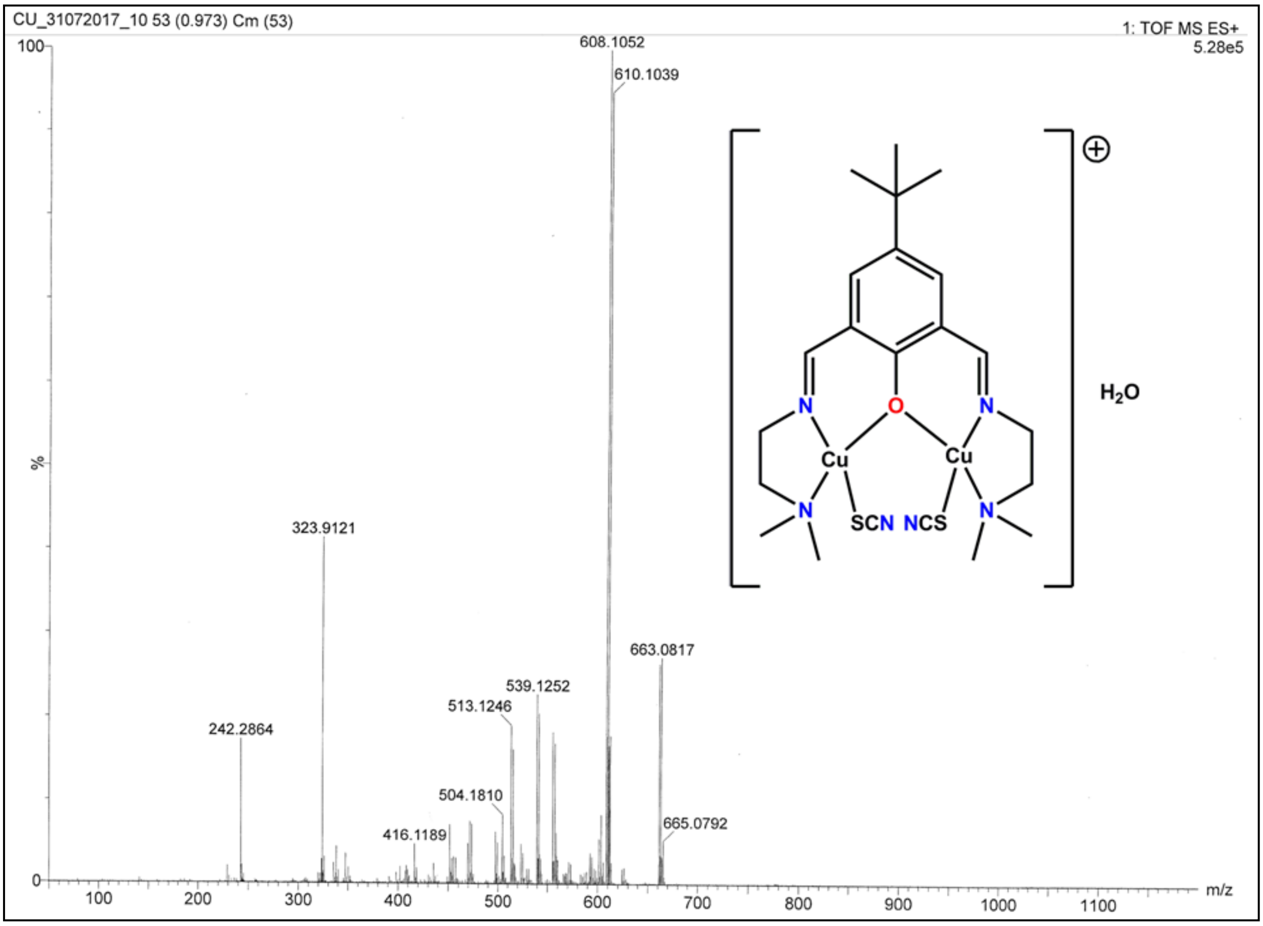


Fig. S4 ESI-MS spectrum of complex **2**

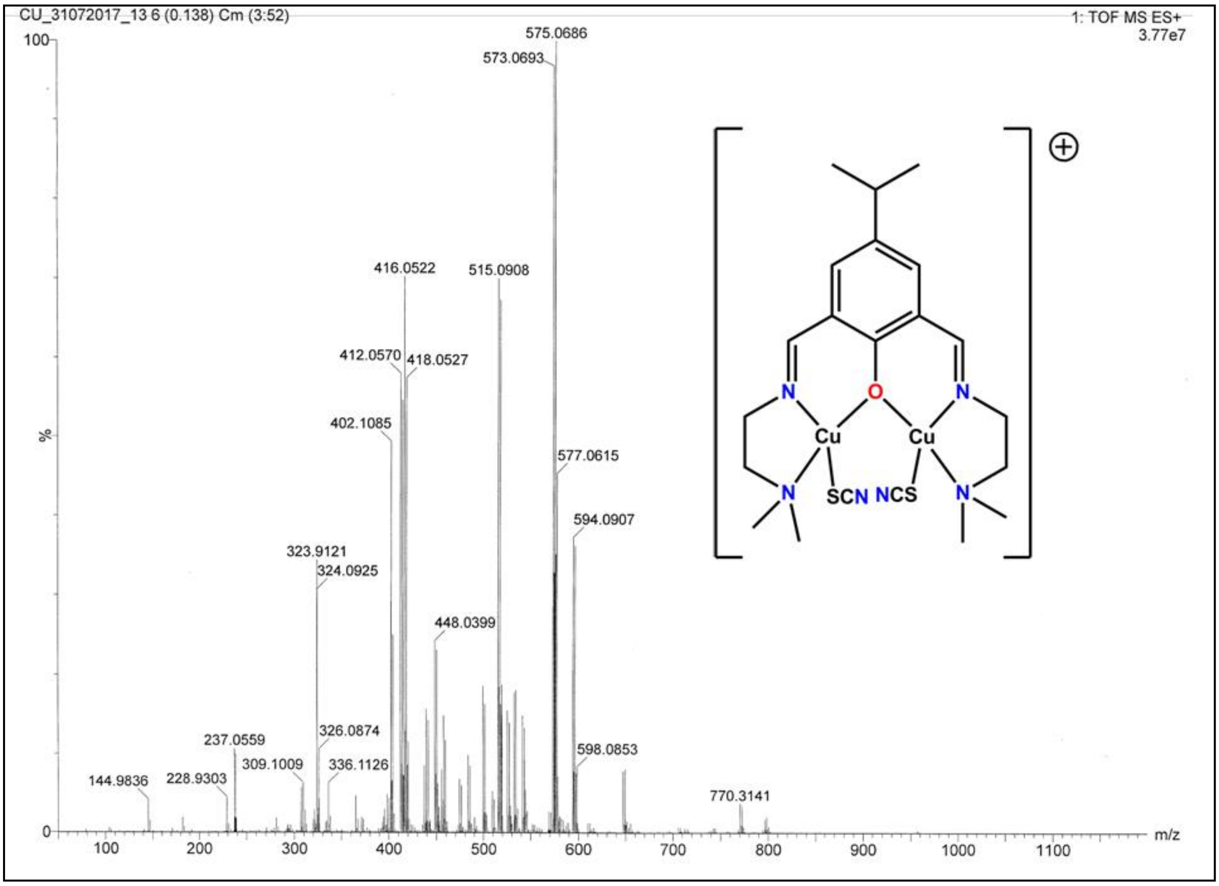


Fig. S5 ESI-MS spectrum of complex **3**

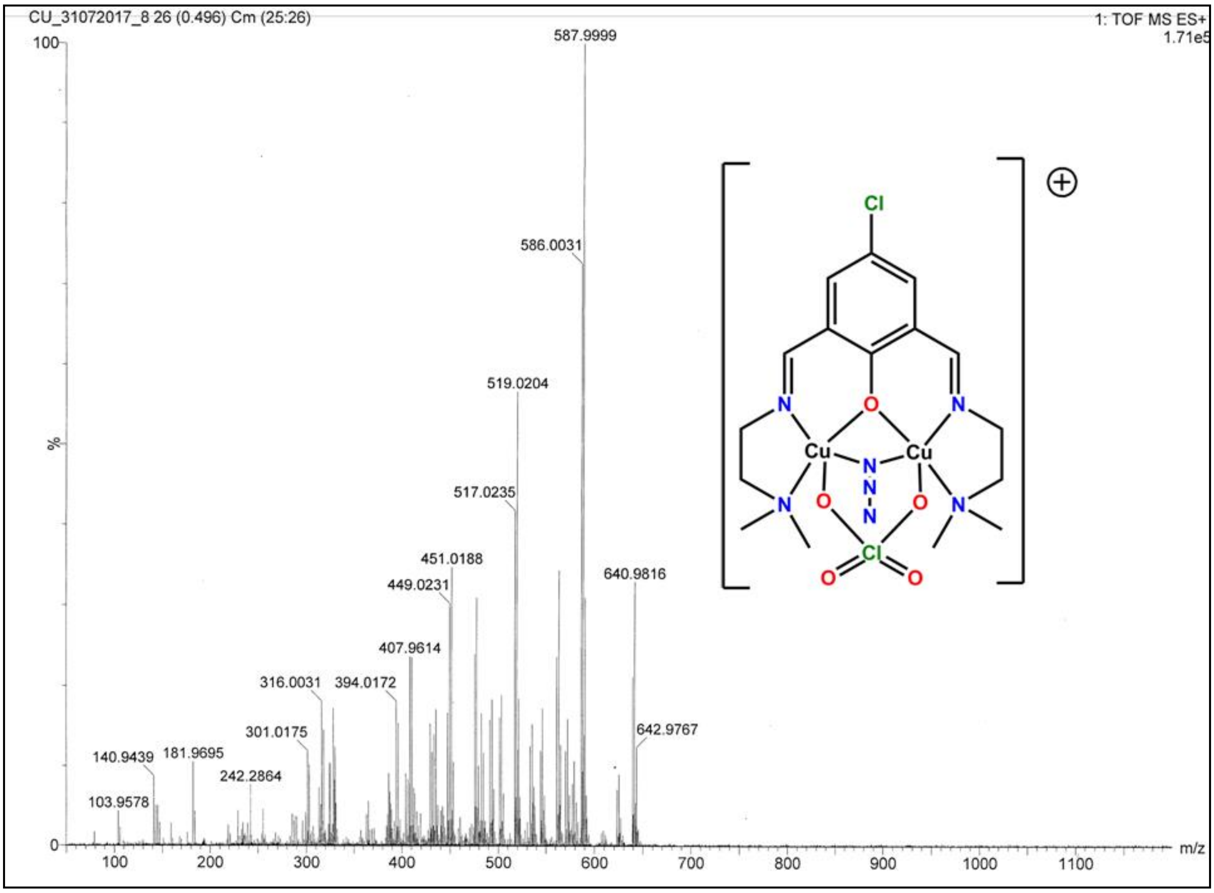


Fig. S6 ESI-MS spectrum of complex **4**

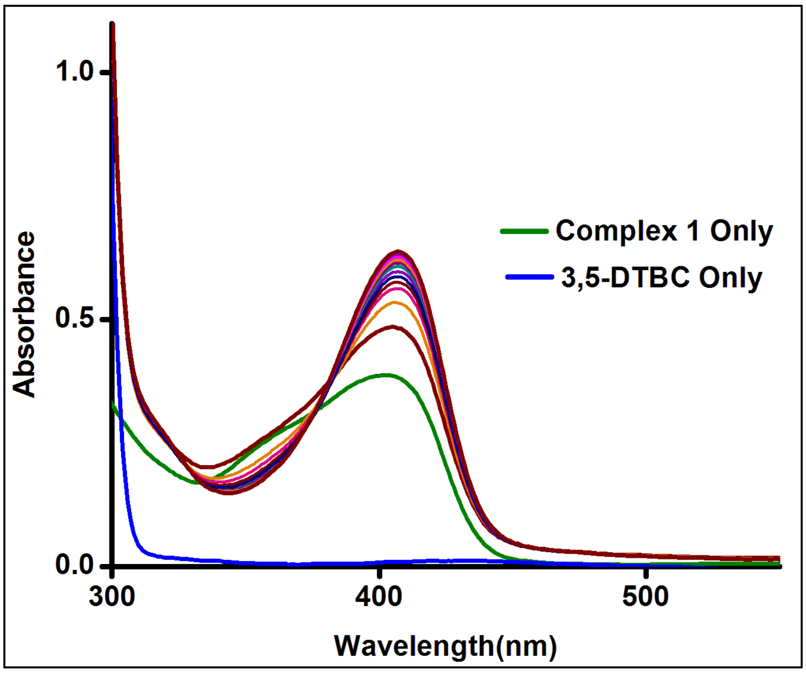


Fig. S7 Oxidation of 3,5-DTBC by complex **1** (substrate: catalyst = 100:1) in DMSO observed by UV-Vis spectroscopy with time at 25 °C at intervals of 5 min.

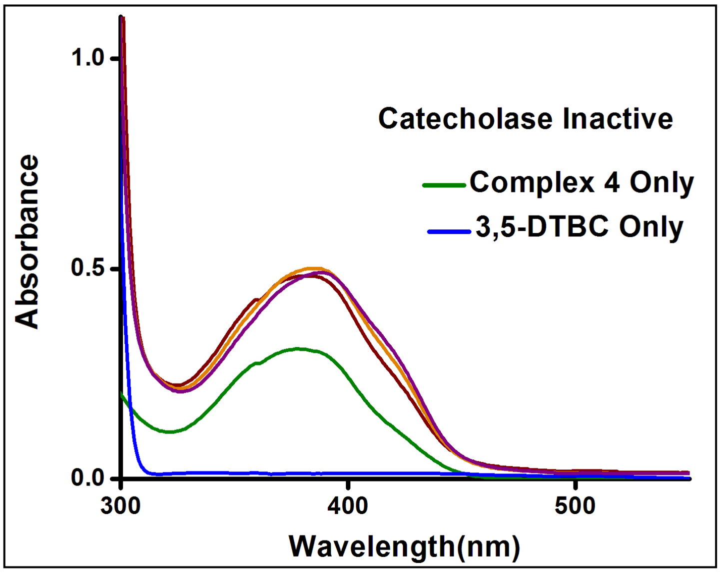


Fig. S8 Oxidation of 3,5-DTBC by complex **4** (substrate: catalyst = 100:1) in DMSO observed by UV-Vis spectroscopy with time at 25 °C .

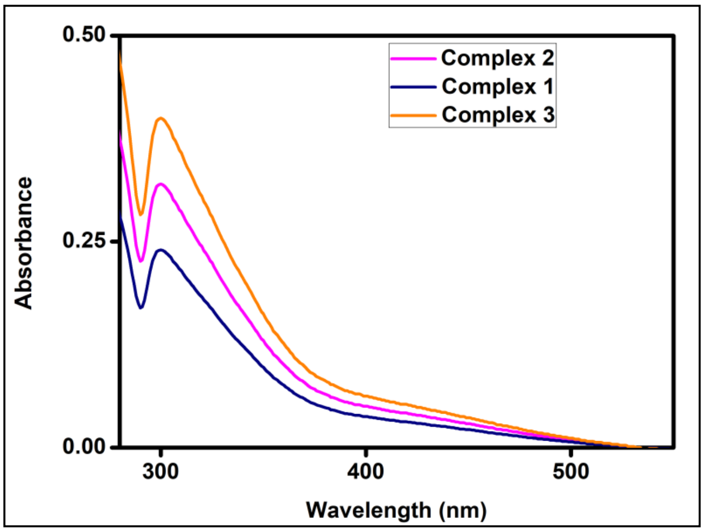


Fig. S9 UV-Vis Spectral scan for determination of I_3^- as a consequence of hydrogen peroxide formation.

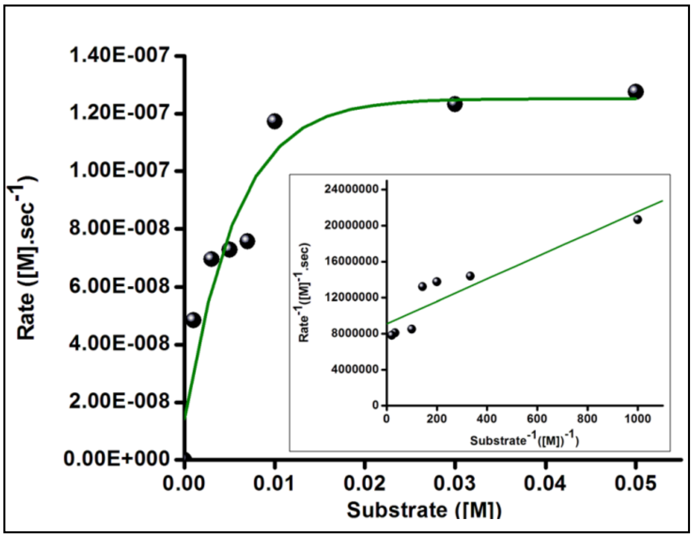


Fig. S10 Lineweaver-Burk plot of complex **1** (Inset shows Plot of enzymatic kinetics for complex **1**) for catecholase activity.

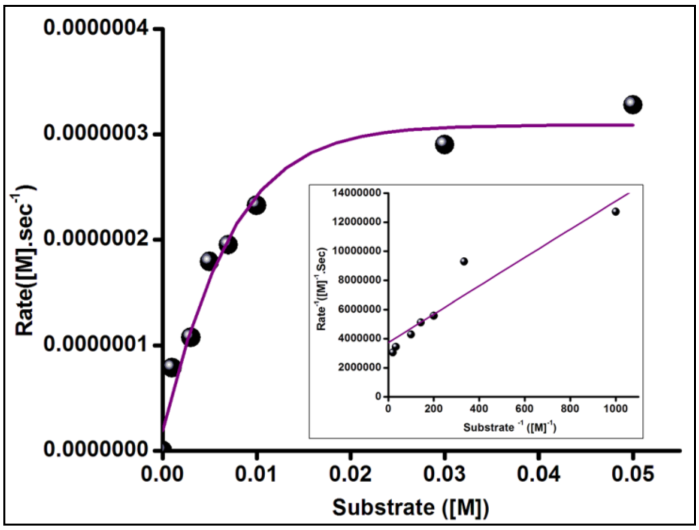


Fig. S11 Lineweaver-Burk plot of complex **2** (Inset shows Plot of enzymatic kinetics for complex **2**) for catecholase activity.

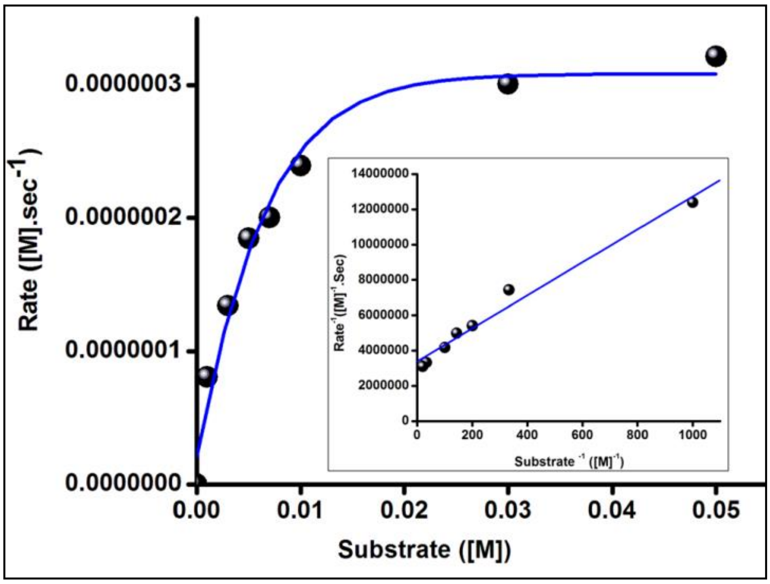


Fig. S12 Lineweaver-Burk plot of complex **3** (Inset shows Plot of enzymatic kinetics for complex **3**) for catecholase activity.