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Varying structural motifs, unusual X-band electron paramagnetic spectra, DFT studies and superoxide dismutase enzymatic activity of copper(II) complexes with N'-[(E)-phenyl(pyridin-2-yl)methylidene]benzohydrazide

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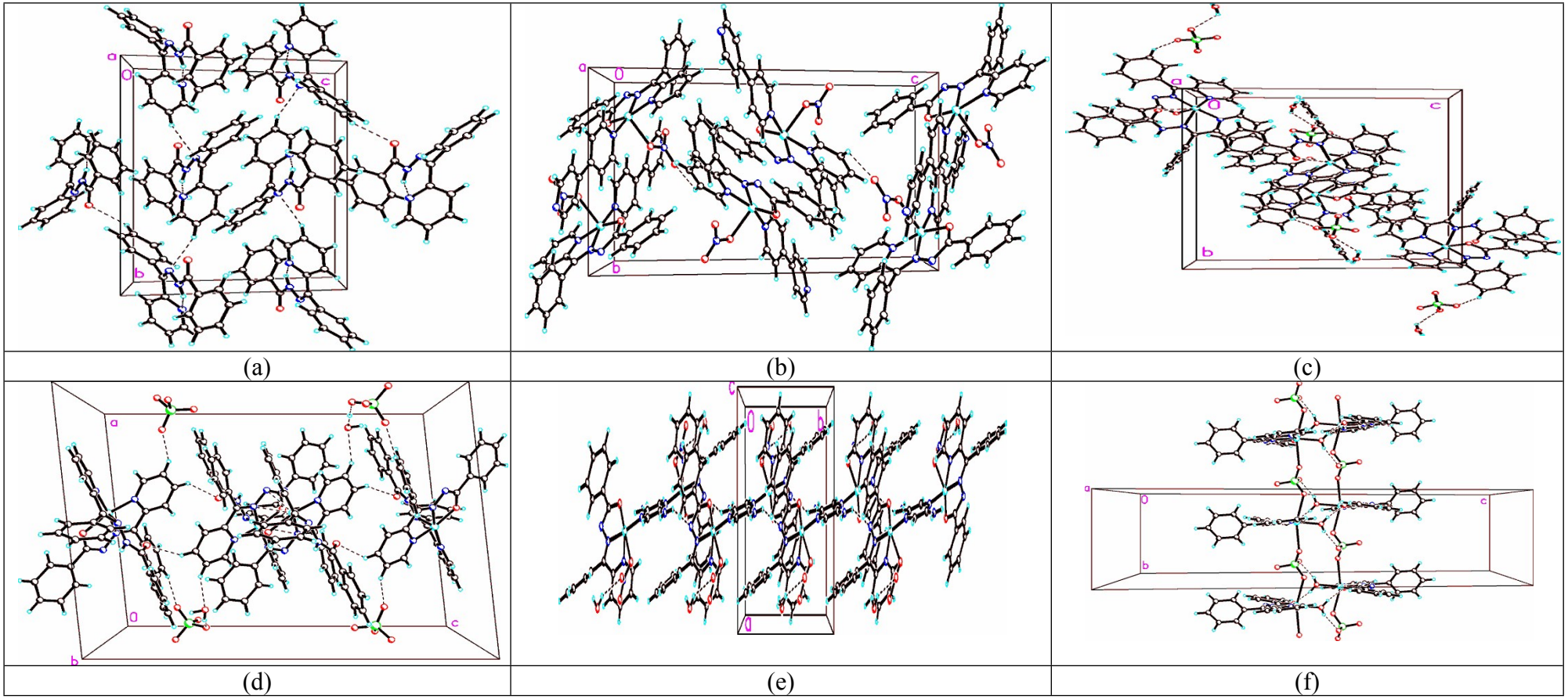


Fig. S1 (a) Inter- and intramolecular interactions in **HL.** (b) Intermolecular interaction in complex **1.** (c) Inter- and intramolecular interaction in complex **2.** (d) Inter- and intramolecular interaction in complex **3.** (e) Inter- and intramolecular interaction in complex **4.** (f) Inter- and intramolecular interaction in complex **5.**

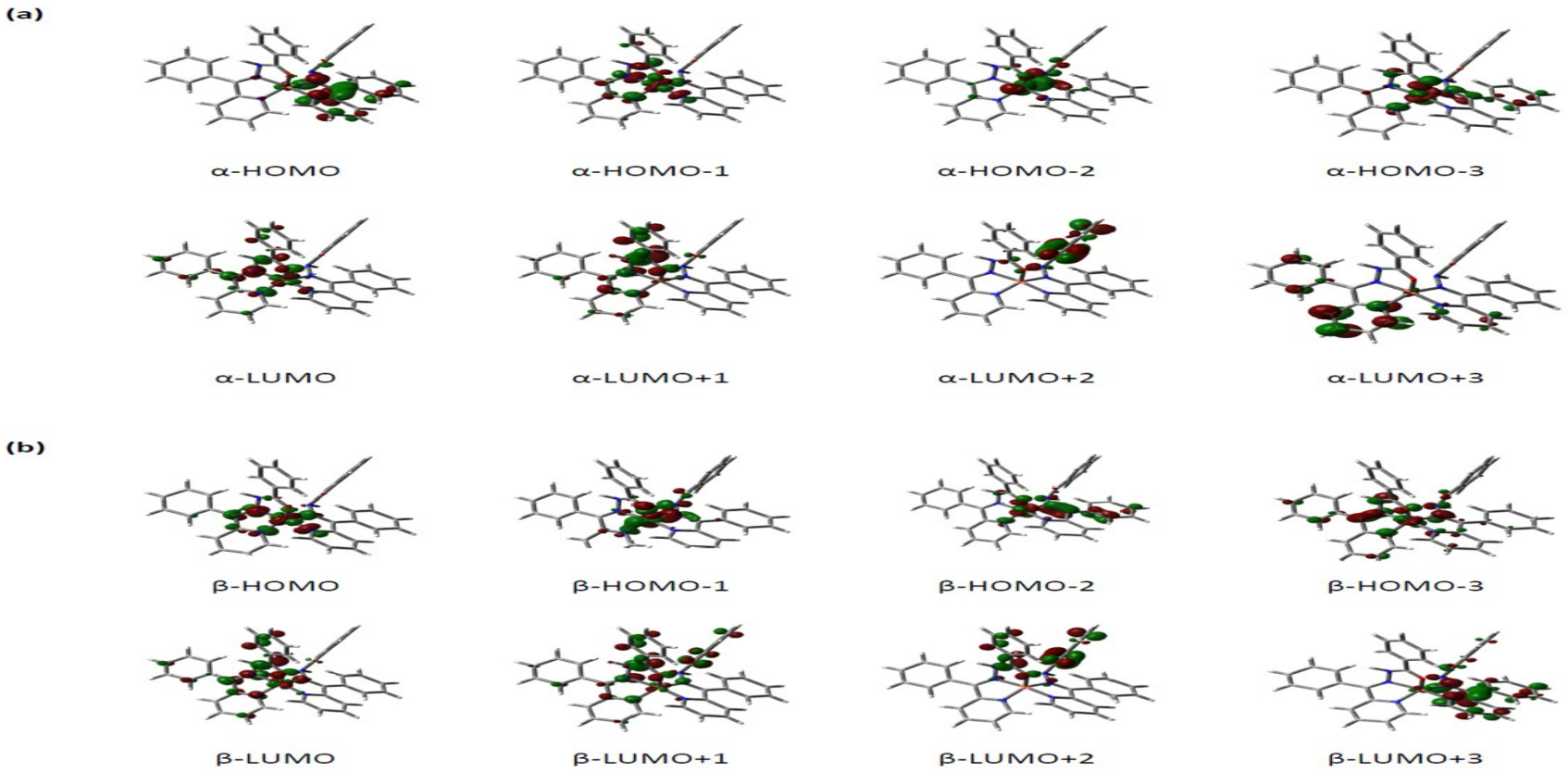
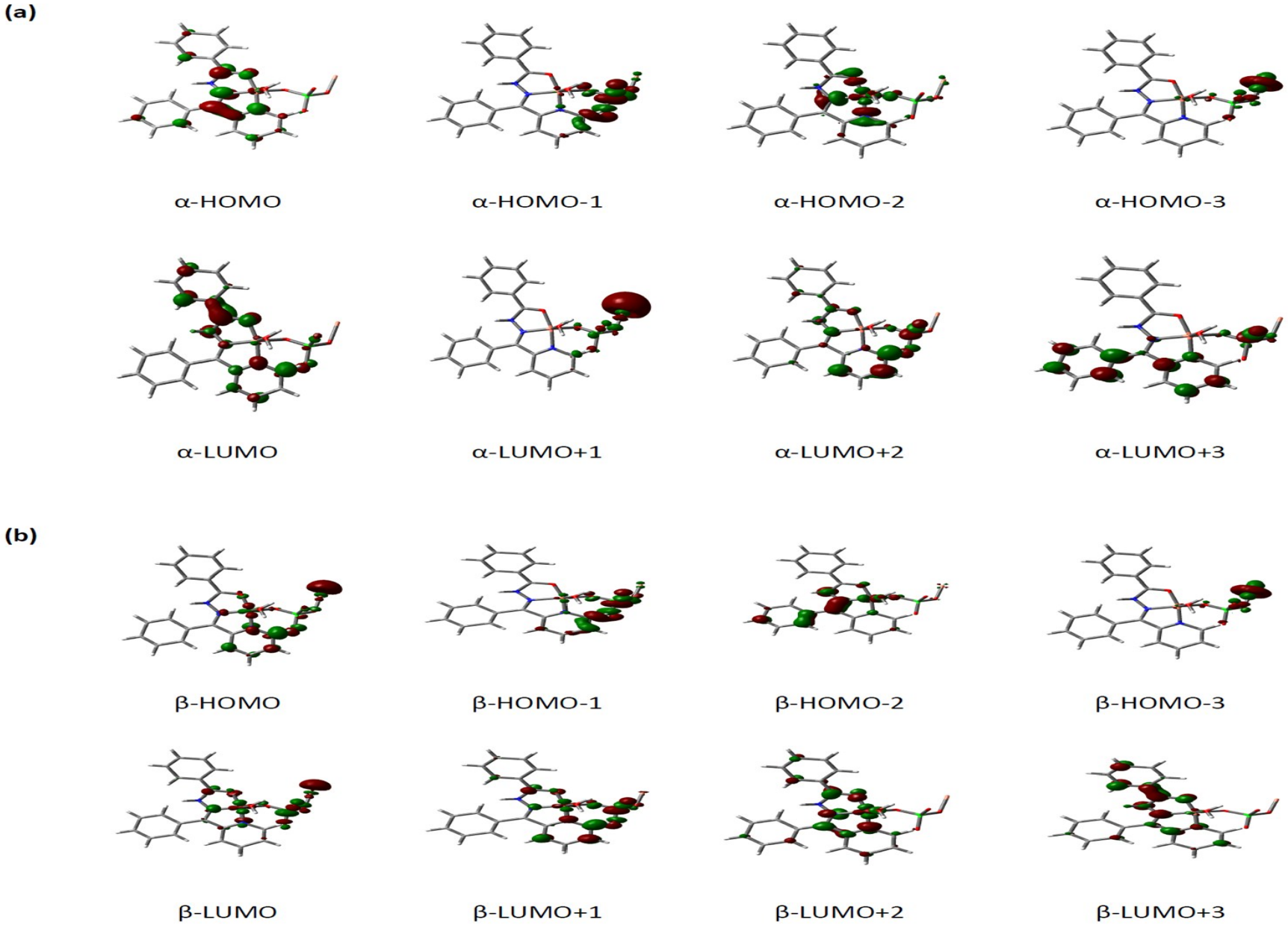


Fig. S2. (a) Some selected frontier plots of MO's (α-spin) of **2.** (b) Some selected frontier Plots of some selected MO's (β-spin) of **3.**



Figue S3. (a) Some selected frontier plots of MO's (α-spin) of **5.** (b) Some selected frontier Plots of some selected MO's (β-spin) of **5.**

Table S1. Selected bond lengths [Å] and angles [°] refer to **1-5**.

Parameters	Single crystal XRD data	Theoretical data	Parameters	Single crystal XRD data	Theoretical data
1					
Cu-N(2)	1.924(2)	2.108	Cu-O(1)	1.9818(18)	2.989
Cu-N(4)	1.983(2)	2.098	Cu-N(1)	2.023(2)	2.146
Cu-O(11)	2.259(2)	2.387			
N(2)-Cu-O(1)	79.67(8)	80.98	N(2)-Cu-N(4)	167.79(9)	168.98
O(1)-Cu-N(4)	97.32(8)	98.48	N(2)-Cu-N(1)	80.36(9)	81.96
O(1)-Cu-N(1)	159.83(8)	161.03	N(4)-Cu-N(1)	101.61(9)	102.91
N(2)-Cu-O(11)	105.31(8)	106.45	O(1)-Cu-O(11)	98.23(8)	90.29
N(4)-Cu-O(11)	86.80(8)	87.89	N(1)-Cu-O(11)	89.77(9)	91.07
2					
Cu-N(2B)	1.929(2)	2.108	Cu-O(1B)	1.977(2)	2.120
Cu-N(1A)	1.997(2)	2.198	Cu-N(1B)	2.007(2)	2.145
Cu-N(2A)	2.389(2)	2.408			
N(2B)-Cu-O(1B)	79.75(9)	80.93	N(2B)-Cu-N(1A)	171.70(9)	171.70
O(1B)-Cu-N(1A)	97.17(9)	98.46	N(2B)-Cu-N(1B)	80.95(10)	80.95
O(1B)-Cu-N(1B)	160.08(9)	161.48	N(1A)-Cu-N(1B)	101.27(9)	101.27
N(2B)-Cu-N(2A)	112.44(9)	113.49	N(1A)-Cu-N(2A)	74.49(8)	74.49
O(1B)-Cu-N(2A)	82.06(8)	83.38	N(1B)-Cu-N(2A)	110.03(9)	111.45
3					
Cu(1)-N(5A)	1.927(2)	2.229	Cu(1)-O(2A)	1.9746(18)	2.198
Cu(1)-N(1A)	1.997(2)	2.108	Cu(1)-N(4A)	2.004(2)	2.215
Cu(1)-N(2A)	2.387(2)	2.456	Cu(2)-N(5B)	1.924(2)	2.145
Cu(2)-O(2B)	1.9798(18)	2.128	Cu(2)-N(1B)	1.989(2)	2.178
Cu(2)-N(4B)	2.006(2)	2.204	Cu(2)-N(2B)	2.390(2)	2.509
N(5A)-Cu(1)-O(2A)	79.71(8)	80.45	N(5A)-Cu(1)-N(1A)	170.57(9)	171.87
O(2A)-Cu(1)-N(1A)	97.85(8)	98.45	N(5A)-Cu(1)-N(4A)	80.92(9)	81.73
O(2A)-Cu(1)-N(4A)	160.08(8)	161.47	N(1A)-Cu(1)-N(4A)	100.52(9)	101.67
N(5A)-Cu(1)-N(2A)	114.11(8)	115.54	O(2A)-Cu(1)-N(2A)	81.76(7)	82.46
N(1A)-Cu(1)-N(2A)	74.27(8)	75.29	N(4A)-Cu(1)-N(2A)	110.62(8)	111.72
N(5B)-Cu(2)-O(2B)	79.81(8)	80.41	N(5B)-Cu(2)-N(1B)	172.48(8)	173.58
O(2B)-Cu(2)-N(1B)	96.46(8)	97.64	N(5B)-Cu(2)-N(4B)	80.96(9)	81.87
O(2B)-Cu(2)-N(4B)	160.18(8)	161.58	N(1B)-Cu(2)-N(4B)	102.07(9)	103.45
N(5B)-Cu(2)-N(2B)	111.26(8)	112.46	O(2B)-Cu(2)-N(2B)	82.49(7)	83.89
N(1B)-Cu(2)-N(2B)	74.45(8)	75.62	N(4B)-Cu(2)-N(2B)	109.12(8)	111.15
C(32B)-O(2B)-Cu(2)	109.67(15)	110.57			
Compound **4**					

Cu-N(2)	1.920(5)	2.124	Cu-O(1)	1.963(4)	2.145
Cu-N(5)	1.988(5)	2.184	Cu-N(1)	2.020(5)	2.132
Cu-O(11B)	2.31(5)	2.398	Cu-O(11A)	2.31(2)	2.38
N(2)-Cu-O(1)	80.29(18)	81.69	N(2)-Cu-N(5)	174.4(2)	175.7
O(1)-Cu-N(5)	94.41(19)	95.72	N(2)-Cu-N(1)	80.6(2)	81.6
O(1)-Cu-N(1)	160.46(17)	161.57	N(5)-Cu-N(1)	104.5(2)	105.7
N(2)-Cu-O(11B)	92.0(10)	94.03	O(1)-Cu-O(11B)	99.1(10)	100.5
N(5)-Cu-O(11B)	90.5(10)	91.50	N(1)-Cu-O(11B)	85.8(10)	86.7
N(2)-Cu-O(11A)	93.9(4)	94.068	O(1)-Cu-O(11A)	90.0(6)	91.8
N(5)-Cu-O(11A)	87.8(4)	89.02	N(1)-Cu-O(11A)	95.5(5)	96.6
Compound **5**					
Cu(1)-N(2)	1.9109(16)	2.1324	Cu(1)-O(1)	1.9468(14)	2.1765
Cu(1)-O(2)	1.9495(14)	2.1490	Cu(1)-N(1)	1.9850(16)	2.1789
Cu(1)-O(3)	2.5078(17)	2.7012	Cu(1)-O(4)#1	2.5449(16)	2.7080
N(2)-Cu(1)-O(1)	80.38(6)	81.56	N(2)-Cu(1)-O(2)	172.15(7)	174.19
O(1)-Cu(1)-O(2)	98.54(6)	99.65	N(2)-Cu(1)-N(1)	81.49(7)	82.48
O(1)-Cu(1)-N(1)	161.56(7)	162.86	O(2)-Cu(1)-N(1)	99.87(6)	100.86
N(2)-Cu(1)-O(3)	106.53(7)	108.09	O(1)-Cu(1)-O(3)	94.85(6)	95.79
O(2)-Cu(1)-O(3)	81.29(7)	82.56	N(1)-Cu(1)-O(3)	87.12(6)	88.12
N(2)-Cu(1)-O(4)#1	92.55(6)	93.65	O(1)-Cu(1)-O(4)#1	97.88(5)	99.08
O(2)-Cu(1)-O(4)#1	79.86(7)	80.96	N(1)-Cu(1)-O(4)#1	86.21(6)	88.24
O(3)-Cu(1)-O(4)#1	158.60(6)	159.69			

Table S2 Hydrogen bonds for complexes **HL** and **1-5** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)	Symmetry transformations used to generate equivalent atoms
H**L**					
N(3)-H(3N)...N(1)	0.890(17)	1.946(16)	2.6652(14)	136.7(13)	#1 -x+1, y+1/2, -z+1/2
C(2)-H(2A)...N(2)#1	0.95	2.61	3.5133(16)	158.2	
1					
C(1)-H(1A)...N(5)#1	0.95	2.47	3.320(4)	148.8	#1 -x,-y+2,-z+1 #2 -x+1/2,y-1/2,-z+1/2 #3 -x+1,-y+1,-z+1
C(2)-H(2A)...O(13)#2	0.95	2.54	3.195(4)	126.2	
C(20)-H(20A)...N(3)#3	0.95	2.69	3.505(3)	144.7	
C(24)-H(24A)...O(11)	0.95	2.37	2.915(3)	115.7	

2					
C(1A)-H(1A)...N(3B)#1	0.95	2.69	3.487(2)	141.7	#1 -x+1,-y+1,-z+1 #2 -x,y+1/2,-z+1/2 #3 -x,-y,-z+1
C(2B)-H(2B)...O(21^b)#2	0.95	2.48	3.277(6)	141.2	
C(2B)-H(2B)...O(1W)#2	0.95	2.39	3.265(8)	153.6	
O(23^b)-H(1W1)...O(21^b)	1.11	1.56	2.314(10)	119.2	
O(1W)-H(1W1)...O(22^b)#3	0.88	2.34	2.979(11)	130.4	
O(1W)-H(1W1)...O(23^b)	0.88	1.11	1.798(12)	129.4	
O(21^b)-H(1W2)...O(23^b)	0.65	1.85	2.314(10)	128.5	
O(1W)-H(1W2)...O(11^a)	0.83	2.35	2.865(10)	120.6	
O(1W)-H(1W2)...O(24^b)	0.83	1.98	2.438(12)	113.4	
O(1W)-H(1W2)...Cl(3^c)	0.83	2.23	2.955(14)	144.9	
O(1W)-H(1W2)...O(31^c)	0.83	1.10	1.92(2)	168.5	
O(1W)-H(1W2)...O(34^c)	0.83	2.63	3.12(3)	118.7	
3					
C(1A)-H(1AA)...N(6A)#1	0.95	2.67	3.475(3)	143.2	#1 -x+1,-y+1,-z+2 #2 x-1/2,-y+1/2,z-1/2
C(21A)-H(21A)...O(21)#2	0.95	2.34	3.176(4)	146.4	#3 -x+1,-y+1,-z+1,#4 x+1/2,-y+1/2,z-1/2
C(1B)-H(1BA)...N(6B)#3	0.95	2.69	3.478(3)	140.7	
C(21B)-H(21B)...O(1W)	0.95	2.44	3.307(4)	151.0	
O(1W)-H(1W1)...O(14)	0.928(19)	2.11(4)	2.904(4)	142(5)	
O(1W)-H(1W2)...O(22)#4	0.901(19)	2.47(6)	2.971(6)	116(5)	
4					
O(1W)-1W1)...O(12A)	0.82(3)	2.74(9)	3.37(3)	134(10)	#1 -x+1,-y+2,-z+1 #2 -x+3/2,y-1/2,-z+3/2 #3 -x+1,-y+1,-z+1
O(1W)-H(1W1)...O(13A)	0.82(3)	2.28(10)	2.97(3)	143(14)	#4 x-1/2,-y+3/2,z-1/2 #5 -x+2,-y+1,-z+1
O(1W)-H(1W1)...O(12B)	0.82(3)	2.15(9)	2.82(4)	139(11)	#6 -+3/2,y+1/2,-z+3/2
O(1W)-H(1W2)...O(11A)#2	0.82(3)	2.41(5)	3.20(2)	162(13)	
O(1W)-H(1W2)...O(13B)#2	0.82(3)	2.36(13)	2.89(5)	124(12)	
N(6)-H(6A)...N(3)#3	0.88	2.20	2.975(11)	146.3	
N(6)-H(6B)...O(1W)#4	0.88	2.25	3.094(14)	159.4	
C(1)-H(1A)...N(6)	0.95	2.60	3.225(12)	123.6	
C(4)-H(4A)...O(12A)#5	0.95	2.63	3.206(12)	119.9	
C(21)-H(21A)...O(1W)#6	0.95	2.37	3.208(10)	147.4	
C(21)-H(21A)...O(11A)	0.95	2.30	2.840(13)	115.3	
5					
C(2)-H(2)...O(5)#2	0.95	2.62	3.226(3)	122.2	#1 x,y-1,z #2 x-1/2,y-1/2,z #3 -x+3/2,-y+3/2,-z+1
O(2)- (102)...O(1)#3	0.82(3)	1.86(3)	2.6663(19)	167(3)	
O(2)- (101)...O(5)#3	0.73(3)	2.12(3)	2.819(2)	162(3)	

Table S3. TD-DFT calculated electronic transitions for the complex **1-3** and **5**

Excitation (eV)	Wavelength (nm)	Oscillator strength (*f*)	Major Contribution	Transition assignment	Exp. Wave length (nm)
			1		
0.2019	870	0.0000	α HOMO → αLUMO (82%)	$d_{yz} \rightarrow d_{x^2-y^2}$	-
0.3263	720	0.0027	αHOMO → αLUMO +1 (41%)	Cu-d $\rightarrow d_{x^2-y^2}$	678
0.3896	530	0.0000	αHOMO-1→αLUMO+1(74%)	LMCT	-
0.5557	395	0.0000	αHOMO → αLUMO +2(61%)	LMCT	420
			2		
0.6724	863	0.0031	α HOMO-3→αLUMO + 1 (47%)	$d_{xz} \rightarrow d_{x^2-y^2}$	-
0.8275	705	0.0300	αHOMO→αLUMO+1 (82%)	$d_{xz} \rightarrow d_{x^2-y^2}$	686
0.8680	460	0.0265	αHOMO-4→ αLUMO (34%)	LMCT	407
0.8871	399	0.0000	αHOMO-1→ αLUMO + 1 (34%)	LMCT	-
			3		
0.2415	843	0.0000	α HOMO-1→αLUMO+1 (63%)	$d_{xz} \rightarrow d_{x^2-y^2}$	-
0.6363	715	0.0000	αHOMO →αLUMO+1 (76%)	$d_{xz} \rightarrow d_{x^2-y^2}$	681
0.8038	465	0.0045	αHOMO-1→ αLUMO (65%)	LMCT	-
0.8873	396	0.0000	αHOMO→ αLUMO +2 (45%)	LMCT	412
			5		
0.6660	833	0.0047	α HOMO→αLUMO+3 (40%)	$d_{xz} \rightarrow d_{x^2-y^2}$	-
0.7857	685	0.0249	αHOMO→αLUMO+1 (41%)	$d_{xz} \rightarrow d_{x^2-y^2}$	677
0.9523	455	0.0707	αHOMO→ αLUMO +2 (59%)	LMCT	420
1.1011	398	0.0060	αHOMO → αLUMO +1 (95%)	LMCT	-

Table S4. Molecular orbital energies and compositions of some selected orbitals for complex **1**

Orbital	Energy (eV)		% of Metal		% of ligand	
	α-spin	β-spin	α-spin	β-spin	α-spin	β-spin
LUMO+9	-0.5553	-0.5553	0	0	100	100
LUMO +8	-1.0267	-1.0267	0	0	100	100
LUMO +7	-1.0811	-1.0811	0	0	100	100
LUMO +6	-1.1091	-1.1091	0	0	100	100
LUMO +5	-1.2607	-1.2607	0	0	100	100
LUMO +4	-1.5181	-1.5181	10	10	90	90
LUMO +3	-1.8419	-1.8419	0	0	100	100
LUMO +2	-2.2538	-2.2538	20	20	80	80
LUMO +1	-2.4101	-2.4101	10	0	90	100
LUMO	-2.7826	-2.7826	10	10	90	90
HOMO	-4.0420.	-4.0420.	45	45	55	55
HOMO-1	-5.1082	-5.1082	15	15	85	85
HOMO-2	-5.4592	-5.4592	60	60	40	40
HOMO-3	-5.6560	-5.6560	10	10	90	90
HOMO-4	-6.2799	-6.2799	49	49	51	51
HOMO-5	-6.5763	-6.5763	50	50	50	50
HOMO-6	-6.6731	-6.6731	0	0	100	100
HOMO-7	-6.8998	-6.8998	60	0	40	100
HOMO-8	-7.0051	-7.0051	60	60	40	40
HOMO-9	-7.2835	-7.2835	40	40	60	60

Table S 5. Molecular orbital energies and compositions of some selected orbitals for complex **2**

Orbital	Energy (eV)		% of Metal		% of ligand	
	α-spin	β-spin	α-spin	β-spin	α-spin	β-spin
LUMO+9	-0.2798	-0.3587	0	0	100	100
LUMO +8	-0.3890	-0.4304	0	0	100	100
LUMO +7	-0.4891	-0.4792	0	0	100	100
LUMO +6	-0.5374	-0.6109	0	0	100	100
LUMO +5	-0.6152	-0.7570	0	0	100	100
LUMO +4	-0.8387	-1.0262	1	1	99	99
LUMO +3	-1.0166	-1.1032	5	5	95	95
LUMO +2	-1.3564	-1.3084	2	5	98	95
LUMO +1	-1.6825	-1.5217	20	20	80	80
LUMO	-1.8152	-1.8080	5	25	95	75
HOMO	-2.8375	-3.5834	50	50	50	50
HOMO-1	-3.1842	-5.2291	80	30	20	70
HOMO-2	-5.1532	-5.6782	20	20	80	80
HOMO-3	-5.9270	-6.1607	15	15	85	85
HOMO-4	-6.2682	-6.4751	10	0	90	100
HOMO-5	-6.5085	-6.6404	15	15	85	85
HOMO-6	-6.7294	-6.6535	10	10	90	90
HOMO-7	-6.7691	-6.7852	15	10	85	90
HOMO-8	-6.9600	-6.9167	20	30	80	70
HOMO-9	-6. 9596	-6.9555	15	10	85	90

Table S6. Molecular orbital energies and compositions of some selected orbitals for complex **3**

Orbital	Energy (eV)		% of Metal		% of ligand	
	α-spin	β-spin	α-spin	β-spin	α-spin	β-spin
LUMO+9	-0.2789	-0.3578	0	0	100	100
LUMO +8	-0.3809	-0.4340	0	0	100	100
LUMO +7	-0.4819	-0.4729	0	0	100	100
LUMO +6	-0.5347	-0.6190	0	0	100	100
LUMO +5	-0.6125	-0.7507	0	0	100	100
LUMO +4	-0.8378	-1.0226	1	1	99	99
LUMO +3	-1.0166	-1.1023	5	5	95	95
LUMO +2	-1.3546	-1.3048	2	5	98	95
LUMO +1	-1.6852	-1.5271	20	20	80	80
LUMO	-1.8125	-1.8008	5	25	95	75
HOMO	-2.8357	-3.5843	50	50	50	50
HOMO-1	-3.1824	-5.2219	80	30	20	70
HOMO-2	-5.1523	-5.6728	20	20	80	80
HOMO-3	-5.9207	-6.1670	15	15	85	85
HOMO-4	-6.2628	-6.4715	10	0	90	100
HOMO-5	-6.5058	-6.6440	15	15	85	85
HOMO-6	-6.7249	-6.6553	10	10	90	90
HOMO-7	-6.7619	-6.7825	15	10	85	90
HOMO-8	-6.9006	-6.9167	20	30	80	70
HOMO-9	-6.9695	-6.95556	15	10	85	90

Table S 7. Molecular orbital energies and compositions of some selected orbitals for complex **5**

Orbital	Energy (eV)		% of Metal		% of ligand	
	α-spin	β-spin	α-spin	β-spin	α-spin	β-spin
LUMO+9	0.2479	0.2274	0	0	100	100
LUMO +8	0.1779	0.0117	0	0	100	100
LUMO +7	0.0446	-0.7205	0	0	100	100
LUMO +6	-0.7692	-0.7545	0	0	100	100
LUMO +5	-0.8253	-0.7793	0	0	100	100
LUMO +4	-0.8566	-0.9477	0	0	100	100
LUMO +3	-1.1273	-1.7105	0	15	100	85
LUMO +2	-2.0441	-2.1296	0	30	100	70
LUMO +1	-2.1647	-2.3881	80	20	20	80
LUMO	-2.3141	-2.7056	5	15	95	85
HOMO	-3.6798	-3.5492	5	40	95	60
HOMO-1	-5.0385	-5.0015	10	5	05	99
HOMO-2	-6.3148	-6.4525	30	10	70	90
HOMO-3	-6.6832	-6.7855	10	1	90	99
HOMO-4	-6.7795	-7.0185	20	2	80	98
HOMO-5	-6.9943	-7.1709	100	80	0	20
HOMO-6	-7.1314	-7.3292	100	100	0	0
HOMO-7	-7.1330	-7.2190	100	80	0	20
HOMO-8	-7.2057	-7.2438	50	45	50	55
HOMO-9	-7. 2451	-7.3075	30	45	70	55