Synergistic Effects of Steric Constraints and Non-covalent Interactions in Copper(II) Chloro-Nitro-Benzoato Complexes: Synthesis, Structural Characterization, Theoretical Investigations, Antimicrobial Studies, and Molecular Docking Analyses

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Supplementary Information

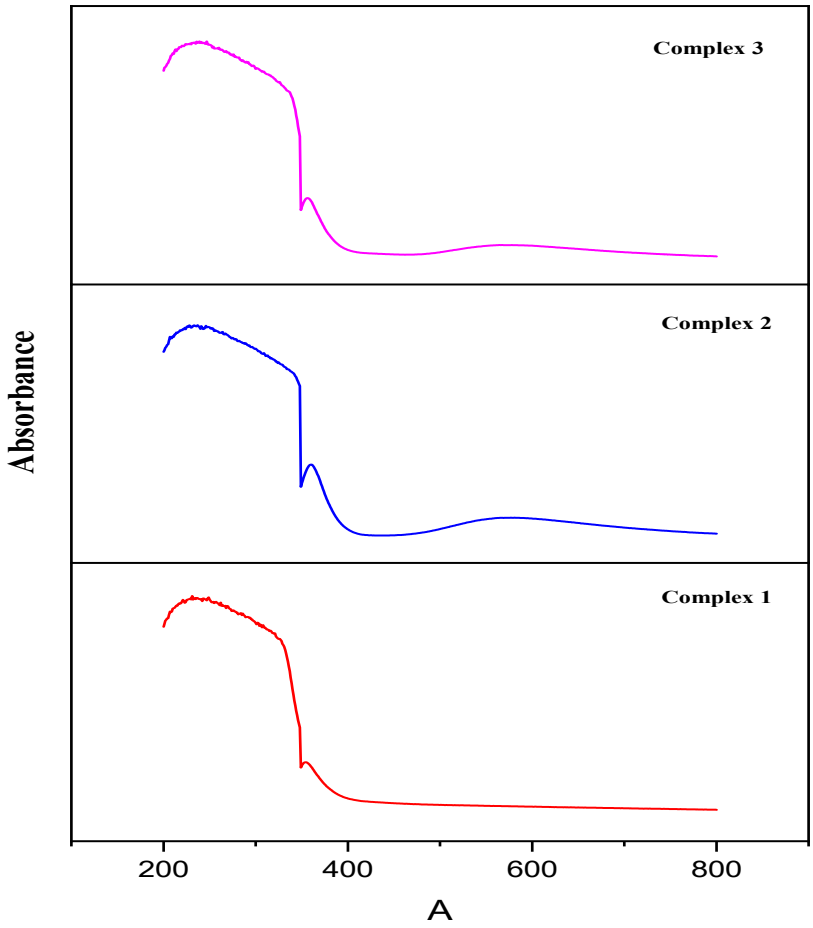

Figure S1: UV spectra of complexes 1-3

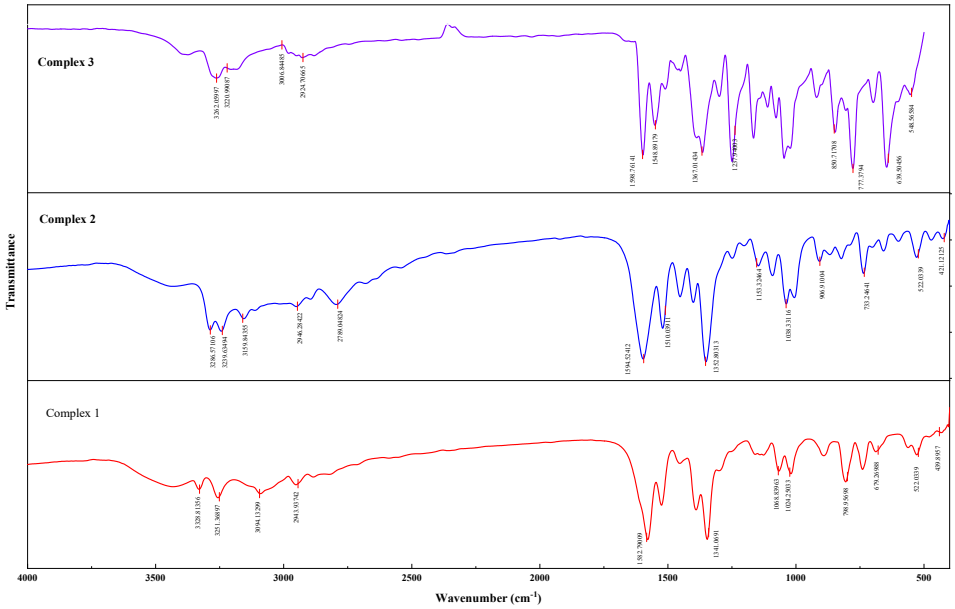

Figure S2 Experimental FT-IR spectra of complexes 1-3

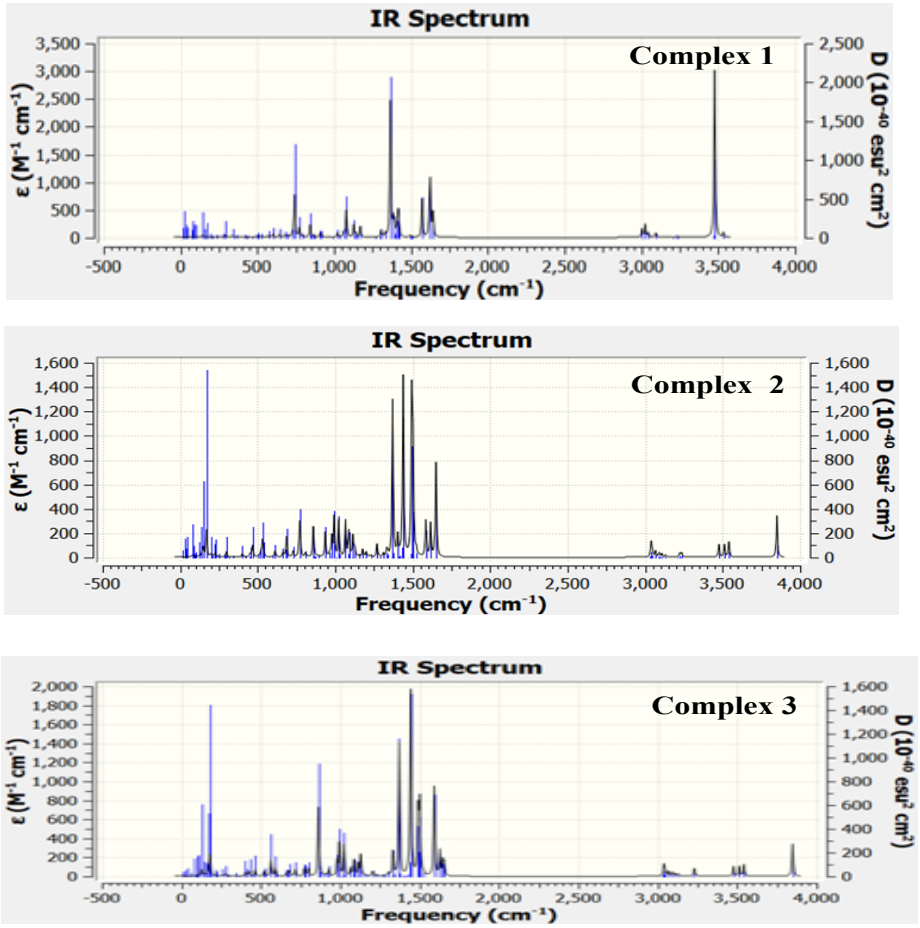

Figure S3: Theoretical elucidation of FT-IR from DFT calculations for complexes 1-3.

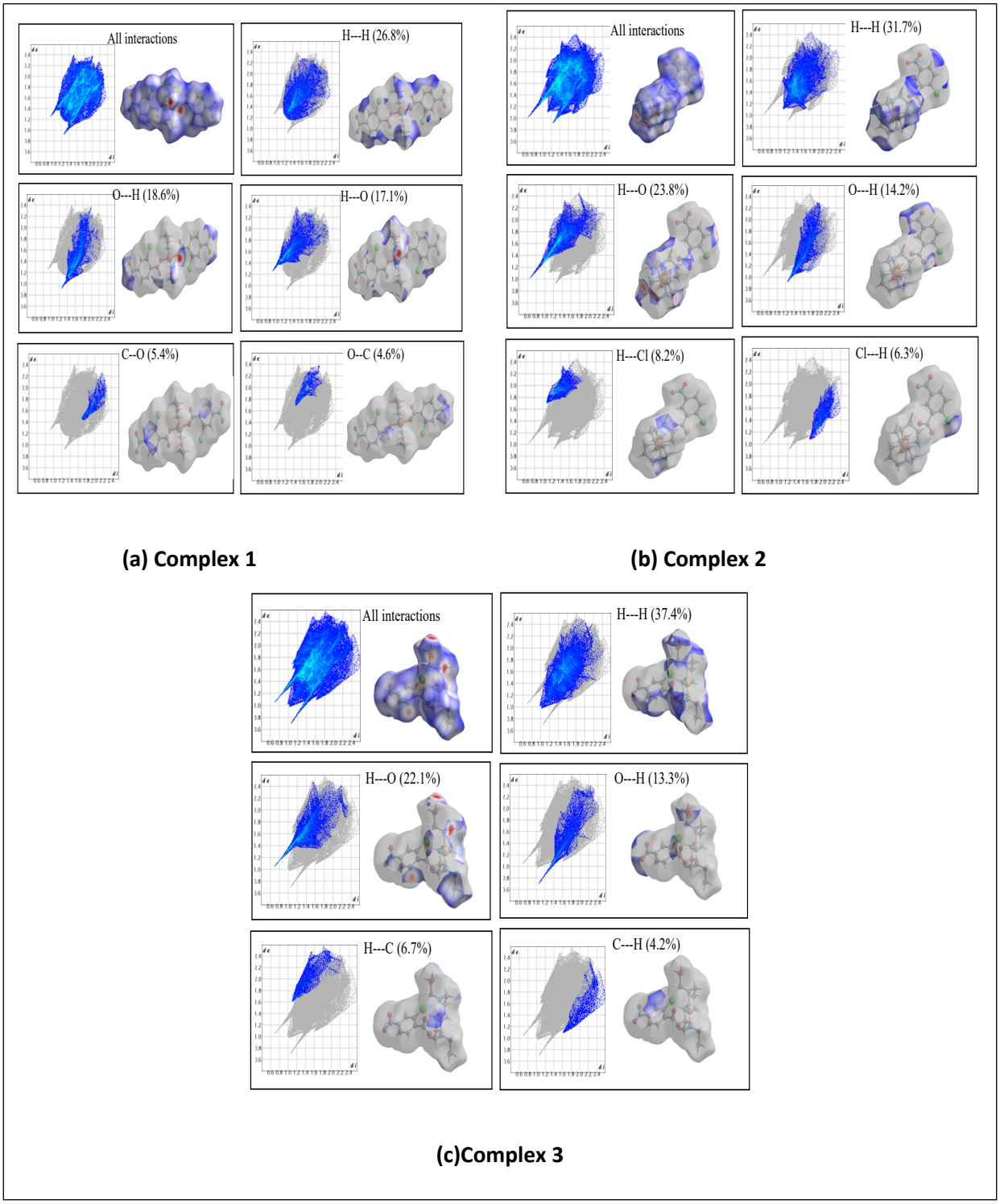

Figure S4: Fingerprint plots of various non-covalent interactions in complexes 1-3 single crystals.

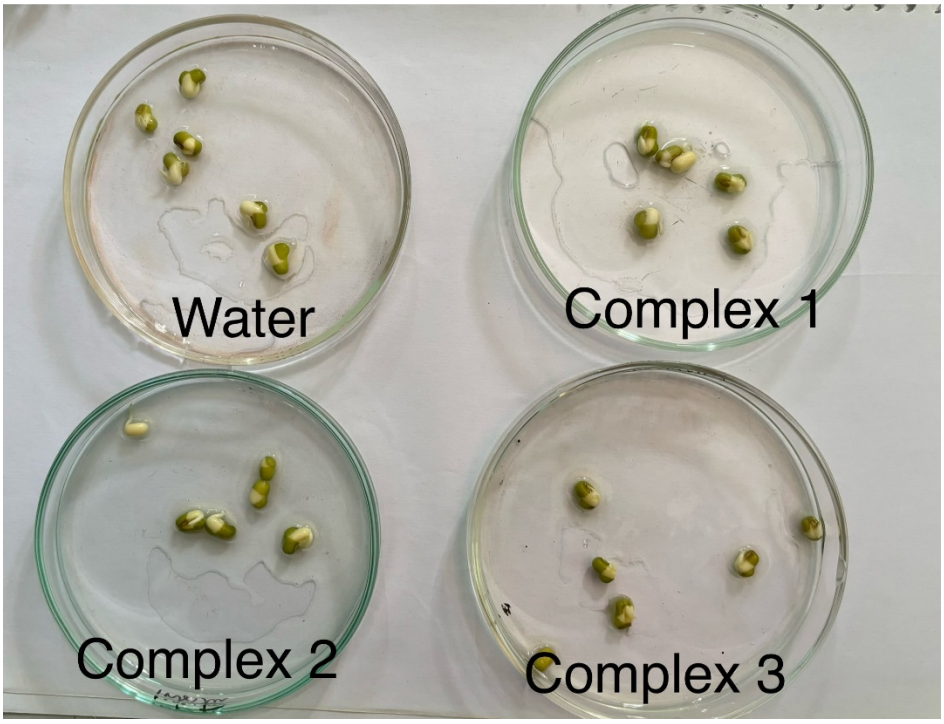

Figure S5: Phytotoxicity assessment: seed germination assay of *Vigna radiata* with Complexes **1-3**.

Table S1 (a) Bond Lengths for Complex 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	O1[1]	2.402(2)	O5	N2	1.217(3)
Cu1	O1	2.402(2)	N1	C2	1.472(4)
Cu1	O2[1]	2.061(2)	N2	C7	1.483(4)
Cu1	O2	2.061(2)	C1	C2	1.494(5)
Cu1	N1[1]	1.983(2)	C3	C4	1.512(4)
Cu1	N1	1.983(2)	C4	C5	1.401(4)
Cl1	C5	1.738(3)	C4	C9	1.393(4)
O1	C1	1.427(4)	C5	C6	1.377(4)
O2	C3	1.271(3)	C6	C7	1.389(4)
O3	C3	1.236(4)	C7	C8	1.370(4)
O4	N2	1.210(3)	C8	C9	1.378(4)

[1]-X,1-Y,2-Z

Table S2 (b) Bond Angles for Complex 1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Cu1	O1[1]	180.00(9)	O4	N2	C7	118.8(3)
O2	Cu1	O1[1]	86.33(7)	O5	N2	C7	117.7(3)
O2[1]	Cu1	O1[1]	93.67(7)	O1	C1	C2	112.1(3)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	Cu1	O1	93.67(7)	N1	C2	C1	110.8(3)
O2[1]	Cu1	O1	86.33(7)	O2	C3	C4	116.9(3)
O2	Cu1	O2[1]	180.0	O3	C3	O2	126.3(3)
N1[1]	Cu1	O1[1]	80.24(9)	O3	C3	C4	116.8(3)
N1	Cu1	O1	80.24(9)	C5	C4	C3	124.6(3)
N1[1]	Cu1	O1	99.76(9)	C9	C4	C3	117.9(3)
N1	Cu1	O1[1]	99.76(9)	C9	C4	C5	117.5(3)
N1	Cu1	O2[1]	88.82(9)	C4	C5	Cl1	121.0(2)
N1[1]	Cu1	O2[1]	91.18(9)	C6	C5	Cl1	117.1(2)
N1[1]	Cu1	O2	88.82(9)	C6	C5	C4	121.7(3)
N1	Cu1	O2	91.18(9)	C5	C6	C7	117.9(3)
N1[1]	Cu1	N1	180.00(9)	C6	C7	N2	118.1(3)
C1	O1	Cu1	102.10(17)	C8	C7	N2	119.2(3)
C3	O2	Cu1	126.6(2)	C8	C7	C6	122.7(3)
C2	N1	Cu1	111.86(19)	C7	C8	C9	118.1(3)
O4	N2	O5	123.6(3)	C8	C9	C4	122.0(3)

[1]-X,1-Y,2-Z

Table S2 (a) Bond Lengths for Complex 2

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	N1[1]	2.0245(17)	N3	C10	1.467(3)
Cu1	N1	2.0245(17)	C1	C2	1.514(3)
Cu1	N2	2.0373(17)	C3	C4	1.507(3)
Cu1	N2[1]	2.0373(17)	C5	C6	1.523(3)
O1	C4	1.420(3)	C6	C7	1.382(3)
O2	C5	1.242(3)	C6	C11	1.394(3)
O3	C5	1.243(3)	C7	C8	1.391(3)
O4	N3	1.209(3)	C7	Cl1	1.737(2)
O5	N3	1.226(3)	C8	C9	1.375(4)
N1	C1	1.480(3)	C9	C10	1.366(4)
N2	C2	1.482(3)	C10	C11	1.379(3)
N2	C3	1.480(3)			

[1]-X,1-Y,1-Z

Table S2(b) Bond Angles for Complex 2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1[1]	Cu1	N1	180.0	O1	C4	C3	111.72(18)
N1	Cu1	N2[1]	94.31(7)	O2	C5	O3	127.3(2)
N1[1]	Cu1	N2[1]	85.69(7)	O2	C5	C6	117.8(2)
N1[1]	Cu1	N2	94.31(7)	O3	C5	C6	114.9(2)
N1	Cu1	N2	85.69(7)	C7	C6	C5	125.0(2)
N2	Cu1	N2[1]	180.0	C7	C6	C11	117.3(2)
C1	N1	Cu1	109.45(13)	C11	C6	C5	117.7(2)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	N2	Cu1	106.96(13)	C6	C7	C8	122.3(2)
C3	N2	Cu1	111.63(13)	C6	C7	Cl1	121.03(18)
C3	N2	C2	115.99(18)	C8	C7	Cl1	116.65(19)
O4	N3	O5	123.4(2)	C9	C8	C7	119.4(2)
O4	N3	C10	119.0(2)	C10	C9	C8	118.7(2)
O5	N3	C10	117.6(2)	C9	C10	N3	118.8(2)
N1	C1	C2	108.55(18)	C9	C10	C11	122.4(2)
N2	C2	C1	111.07(17)	C11	C10	N3	118.8(2)
N2	C3	C4	113.57(17)	C10	C11	C6	119.8(2)

[1]-X,1-Y,1-Z

Table S3 (a) Bond Lengths for Complex 3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	N1[1]	2.035(3)	N2	C1	1.488(5)
Cu1	N1	2.035(3)	N3	C9	1.473(5)
Cu1	N2	2.025(3)	C1	C2	1.512(6)
Cu1	N2[1]	2.025(3)	C3	C4	1.522(5)
Cl1	C7	1.749(4)	C5	C6	1.517(5)
O1	C4	1.400(5)	C6	C7	1.379(5)
O2	C5	1.232(4)	C6	C11	1.389(5)
O3	C5	1.260(4)	C7	C8	1.382(5)
O4	N3	1.205(5)	C8	C9	1.367(5)
O5	N3	1.224(5)	C9	C10	1.371(5)
N1	C2	1.473(4)	C10	C11	1.394(5)
N1	C3	1.479(4)			

[1]2-X,-Y,1-Z

Table S3 (b) Bond Angles for Complex 3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1[1]	Cu1	N1	180.0	O1	C4	C3	107.7(3)
N2[1]	Cu1	N1	94.64(12)	O2	C5	O3	126.7(3)
N2	Cu1	N1[1]	94.64(12)	O2	C5	C6	117.7(3)
N2[1]	Cu1	N1[1]	85.36(12)	O3	C5	C6	115.6(3)
N2	Cu1	N1	85.36(12)	C7	C6	C5	123.0(3)
N2	Cu1	N2[1]	180.00(11)	C7	C6	C11	117.9(3)
C2	N1	Cu1	106.1(2)	C11	C6	C5	119.0(3)
C2	N1	C3	113.9(3)	C6	C7	Cl1	119.7(3)
C3	N1	Cu1	114.7(2)	C6	C7	C8	122.5(3)
C1	N2	Cu1	109.1(2)	C8	C7	Cl1	117.9(3)
O4	N3	O5	123.5(4)	C9	C8	C7	117.8(4)
O4	N3	C9	118.9(4)	C8	C9	N3	118.5(4)
O5	N3	C9	117.7(4)	C8	C9	C10	122.5(3)
N2	C1	C2	108.5(3)	C10	C9	N3	119.1(3)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C2	C1	109.4(3)	C9	C10	C11	118.5(3)
N1	C3	C4	113.5(3)	C6	C11	C10	120.8(4)

[1]2-X,-Y,1-Z

Table S4: Hydrogen Bonding parameter for Complexes 1-3

Complex 1				
D-H…A	**d(D-H)**	**d(H…A)**	**<D-H…A**	**d(D-A)**
O1-H1…O3	0.820	1.844	170.07	2.655
N1-H1B…O2[a]	0.890	2.292	150.51	3.097
C1-H1C…Cl1[b]	0.970	2.922	158.79	3.842
C2-H2B…O4[c]	0.970	2.528	131.72	3.255
a= -x+1, -y+1, -z+2; b = -x, -y+1, -z+2; c = -x+1, y+1/2, -z+3/2				
Complex 2				
O1-H1…O3[a]	0.82	1.80	172	2.618(2)
N1-H1A…O2[b]	0.89	2.24	159	3.081(3)
N1-H1B…O2[c]	0.89	2.28	149	3.078(2)
N2-H2…Cl1[d]	0.98	2.81	138	3.606(8)
N2-H2…O2[d]	0.98	2.29	144	3.135(3)
C1-H1C…O1[e]	0.97	2.59	161	3.519(3)
C3-H3A…O5[f]	0.97	2.43	135	3.188(3)
C8-H8…O4[g]	0.93	2.39	143	3.185(4)
a = x,y,-1+z; b= -x,1-y,1-z; c = -1+x,y,z; d = 1-x,1-y,1-z; e = -x,2-y,1-z; f = x,y,-1+z; g = 1+x,y,z				
Complex 3				
O1-H1…O3[a]	0.82	1.95	169	2.763(4)
N1-H1A…O1	0.98	2.55	105	2.963(4)
N1-H1A…O3[b]	0.98	2.11	141	2.935(5)
N2-H2A…O2[c]	0.89	2.28	156	3.112(4)
N2-H2B…O3	0.89	2.48	137	3.193(4)
C11-H11…O1[d]	0.93	2.41	168	3.329(5)
a = x,1/2-y,-1/2+z; b = 2-x,-y,1-z; c = x,-1+y,z; d = 2-x,1-y,1-z				

Table S5: Comparative analysis of experimental and theoretical vibrational mode frequencies of complexes 1-3.

Assignments	**COMPLEX 1**		**COMPLEX 2**		**COMPLEX 3**	
	Experimental IR (cm^{-1})	**Calculated (B3LYP/6-311G(d,p)**	**Experimental IR (cm^{-1})**	**Calculated (B3LYP/6-311G(d,p)**	**Experimental IR (cm^{-1})**	**Calculated (B3LYP/6-311G(d,p)**
sp3 (CH)	3328	3467	3286	3235	3262	3230
sp3 (CH)	3094	3093	3159	3131	3006	3038
sp3 (CH)	2943	3003	2946	3033	2924	3033
ν_{as}(COO)	1582	1572	1594	1584	1598	1591
ν_{s}(COO),	1341	1332	1352	1370	1367	1371
C—O stretching	1068	1060	1038	1031	1237	1228
C—O stretching	1024	1021	906	891	850	862
(Cu–N).	522	527	522	520	548	564

Table S6 Some of characteristic examples of complexes having CuN_4O_2 chromophore.

S.No.	Name of complex	Absorption wavelength (nm)	Ref.
1.	[Cu(N-*hyden*)$_2$](o-methoxybz)$_2$	578	[57]
2.	[Cu(N-*hyden*)$_2$](m-methoxybz)$_2$	582	[57]
3.	[Cu(N-*hyden*)$_2$](p-methoxybz)$_2$	580	[57]
4.	[Cu(*en*)$_2$(H_2O)$_2$](m-methoxybz)$_2$	546	[59]
5.	[Cu(*en*)$_2$(H_2O)$_2$](3,4,5-trimethoxybz)$_2$	552	[59]
6.	[Cu(*en*)$_2$(H_2O)$_2$](mef)$_2$	555	[60]
7.	[Cu(N-*hyden*)$_2$]Cl_2	556	[61]
8.	Complex **1**	560	Present work
9.	Complex **2**	575	Present work
10.	Complex **3**	578	Present work

Table S7: calculated Mulliken charges of the atoms in complexes 1-3

Complex 2				Complex 3									
Mulliken Charges	Atom	Mulliken Charges	- Atom	Mulliken Charges	Atom	Mulliken Charges	Atom	Mulliken Charges	Atom	Mulliken Charges	Atom	Mulliken Charges	
0.079	C29	-0.431	C1	-0.140	Cu13	1.145	O35	-0.558					
-0.124	C32	-0.190	C2	0.060	N14	-0.452	O36	-0.553					
-0.017	O35	0.339	C3	-0.201	N16	-0.514							
0.025			C4	0.454	C17	0.268							
0.71			C5	-0.368	C20	0.275							
-0.175			C6	-0.013	C25	0.233							
-0.061			Cl9	-0.276	C28	0.422							
-0.395			C10	1.1531	O31	-0.643							
-0.205			O11	-0.867	N34	1.253							

	Atom	O13	N14	O15	O16	Cu17	N18	N20	C21	C24
	Mulliken Charges	-0.429	0.043	-0.464	-0.160	0.615	-0.423	0.543	-0.603	-0.032
	Atom	C1	C2	C3	C4	C5	C6	Cl10	C11	O12
Complex 1	**Mulliken Charges**	0.202	-0.616	-0.773	0.143	-0.033	-0.304	0.021	-0.343	
	Atom	C12	C13	C14	C15	C16	C18	C20	C22	
	Mulliken Charges	0.232	0.548	-0.088	-0.274	-0.300	-0.234	-0.007	-0.171	-0.004
	Atom	Cu 1	Cl2	O3	O4	O5	N6	O9	N10	O11

Table S8: General surface information for complexes 1-3

General surface information	Complex 1	Complex 2	Complex 3
Iso-value	0.05	0.5	0.5
Volume (Å³)	552.45	471.77	493.20
Area (Å²)	468.53	399.26	424.76
Globularity	0.695	0.734	0.711
Asphericity	0.410	0.177	0.085

Table S9: Surface property information for complexes 1-3

Name (property)	Complex 1			Complex 2			Complex 3		
	Min	**Mean**	**Max**	**Min**	**Mean**	**Max**	**Min**	**Mean**	**Max**
d_i (Å)	0.927	1.689	2.381	0.654	1.591	2.453	0.713	1.620	2.601
d_e (Å)	0.927	1.696	2.403	0.928	1.662	2.463	0.716	1.695	2.611
d_{norm}	-0.316	0.402	1.130	-0.733	0.383	1.092	-0.642	0.447	1.341
Shape index	-0.995	0.209	0.995	-0.990	0.216	0.996	-0.997	0.209	0.999
Curvedness	-4.023	-0.960	0.132	-3.969	-0.927	0.355	-3.708	-0.940	0-359

Table S10: Breaking down the fingerprint by element type, the surface area of close interactions between atoms within and outside of the surface is determined as a proportion of the total surface area for complexes 1-3.

Complex 1	**Inside atom**	**Outside atoms**						
		Cu	**Cl**	**O**	**N**	**H**	**C**	
	C	0	0.7	5.4	0.9	3.9	1.9	12.8
	Cl	0	0	3.2	0.8	4.4	0.7	9.1
	Cu	0	0	0	0	0	0	0
	H	0	2.7	17.1	0.1	26.6	3.2	49.7
	N	0	0.8	0	0	0.1	0.9	1.8
	O	0	2.4	0.4	0	18.6	4.8	26.2
		0	6.6	26.1	1.8	53.6	11.5	
Complex 2	**Inside atom**	**Outside atoms**						
		Cu	**Cl**	**O**	**H**	**N**	**C**	
	C	0	0	2.5	1.9	1.1	1.9	7.9
	Cl	0	0	1.0	6.3	0	0	7.3
	Cu	0	0	0	0	0	0	0
	H	0	8.2	23.8	31.7	0	2.2	65.9
	N	0	0	0	0.1	0	1.0	1.1
	O	0	0.8	1.2	14.2	0	2.2	18.4
		0	9.1	28.4	54.1	1.1	7.3	
Complex 3	**Inside atom**	**Outside atoms**						
		Cu	**O**	**H**	**N**	**C**	**Cl**	
	C	0	1.8	4.2	0	0	0.7	6.7
	Cl	0	0.8	2.0	0.5	0.6	0.8	4.8
	Cu	0	0.7	0	0	0	0	0.7
	H	0	22.1	37.4	0	6.7	3.5	69.6
	N	0	0.5	0	0	0	0.5	1
	O	0	1.2	13.3	0.5	1.5	0.7	17.2
		0	27.1	56.9	1.0	8.8	6.1	

Table S11: Molecular docking of complexes 1-3 against two Gram-positive bacteria (B. Cereus, S. Aureus) with PDB ID (5V8E, 1BDD) respectively and four Gram-negative bacteria (E. Coli, S. Typhi, P. Aeruginosa, S. Flexneri) with PDB ID (1DIH, 1TJY, 6P8U, 5KH1)

Protein (PDB:ID)	Complex 1			Complex 2			Complex 3		
	Binding residues	**Inhibition Constant (µMol)**	**Binding energy (kcal/mol)**	**Binding residues**	**Inhibition Constant (µMol)**	**Binding energy (kcal/mol)**	**Binding residues**	**Inhibition Constant (µMol)**	**Binding energy (kcal/mol)**
5V8E	Lys103 His201 His202 Ser249 Asp314 Asp336 Ser337 Arg359	0.7989	-8.3	Lys103 His201 Phe250 Ser249 Asp313 Asp314 Ser337 Phe338 Arg359 Ser383	1.869	-7.8	Lys103 Ser142 Lys143 His201 Ser385 Asn386 Ser388	0.4797	-8.6
1BDD	Phe6 Gln11 Pro39	10.130	-6.8	Ala2 Asp3 Phe6	23.7008	-6.3	Glut27 Glu48	23.7008	-6.3
1DIH	Arg16 Met17 Arg81 Asn128 Thr170 Arg240 Phe243	0.6740	-8.4	His159 Val217 Arg240 Phe243	7.210	-7.0	Arg16 Met17 Phe79 Asn128 Thr170 Arg240	1.576	-7.9
1TJY	Met106 Lys111 Ser125 Leu282 Gly318	3.081	-7.5	Thr163 Thr165 Lys172 Tyr312	14.232	-6.6	Met106 Glu107 Lys111 Leu282 Met286	1.5765	-7.9
6P8U	Ile81 Tyr83 Lys122	0.946	-8.2	Arg164 Leu207 Glu208 Leu210 Tyr211 Gly213	3.652	-7.4	Gln22 Phe46 Leu47 Tyr51 Ala52 Tyr141 Lys160	2.602	-7.6
5KH1	Glu418 Asp486 Glu487 Arg554 Gln558	3.652	-7.4	Glut193 Leu194 Thr212 Asp213 Pro235	5.132	-7.2	Asp213 Pro215 Phe462 Val465 Ser466 Gly467	0.946	-8.2