Electronic Supporting Information

Synthesis, DNA binding, cellular DNA lesion and cytotoxicity of a series of new benzimidazole-based Schiff base copper(II) complexes

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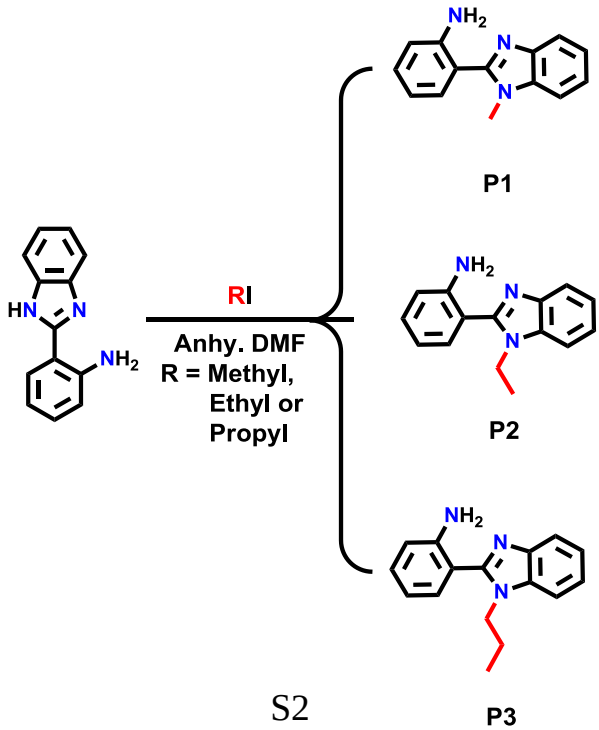
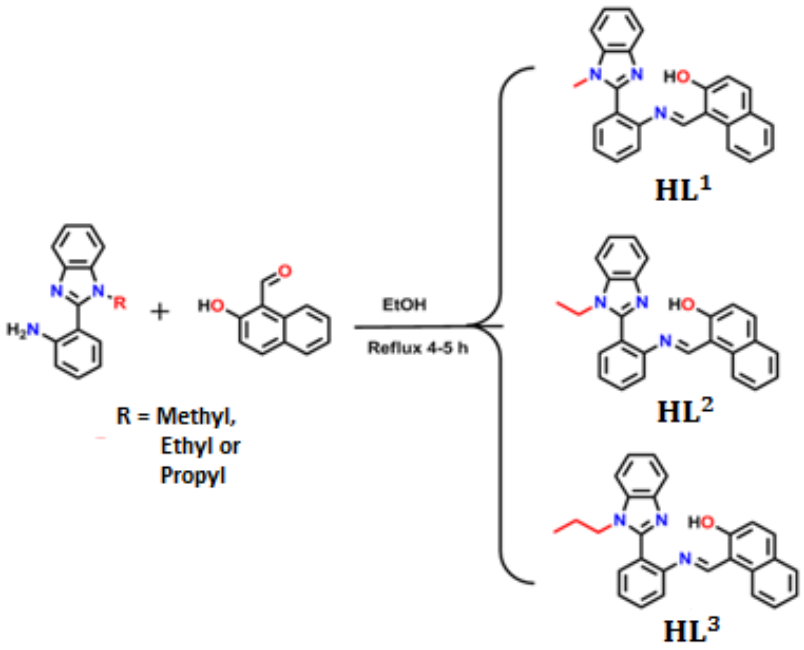
Supplementary Figures **Pages**



Scheme S1.Synthesesof **P1**, **P2** and **P3**.



Scheme S2. Synthesesof **HL¹**, **HL²** and **HL³**.

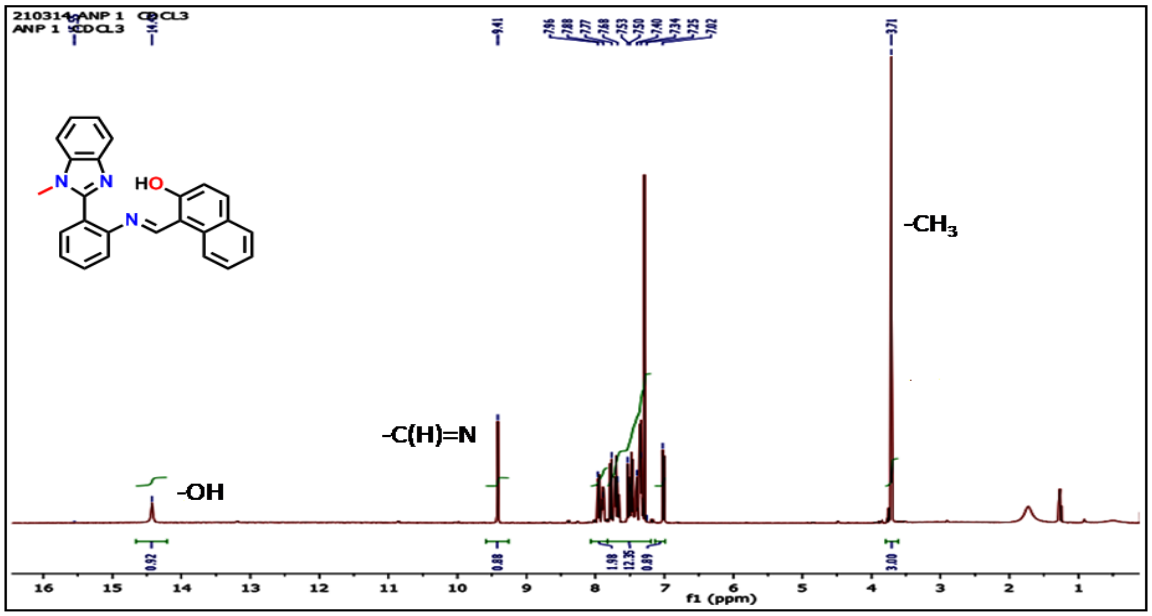


Fig. S1. ^{1}HNMR spectrum of **HL¹**in $CDCl_3$.

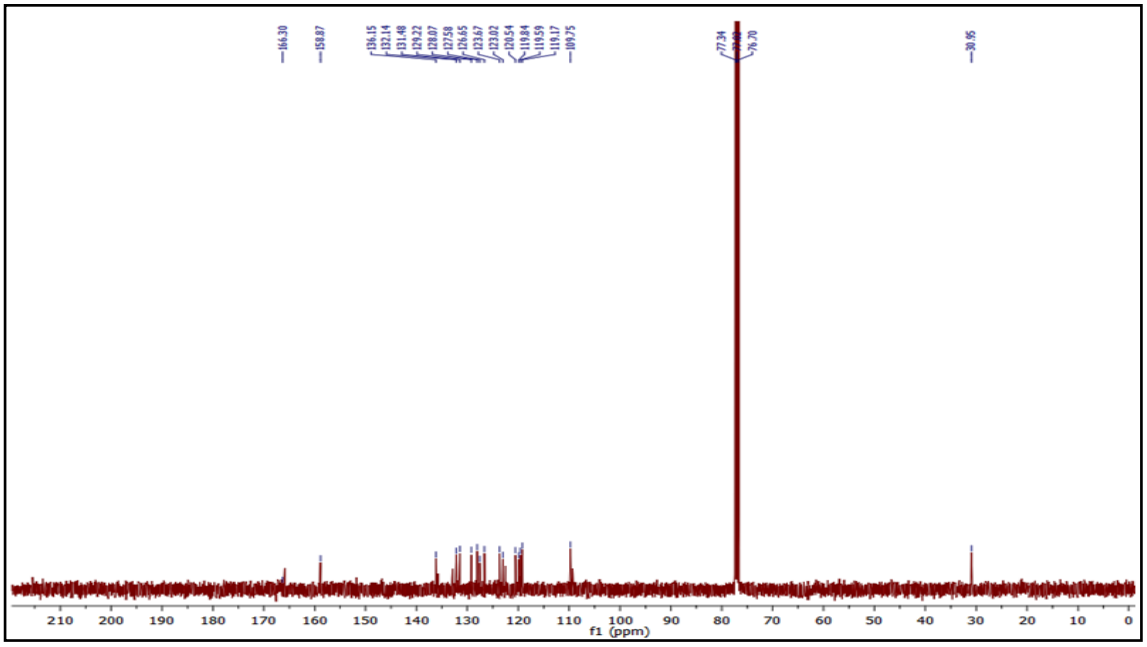


Fig. S2. ^{13}C NMR spectrum of **HL^1**in $CDCl_3$.

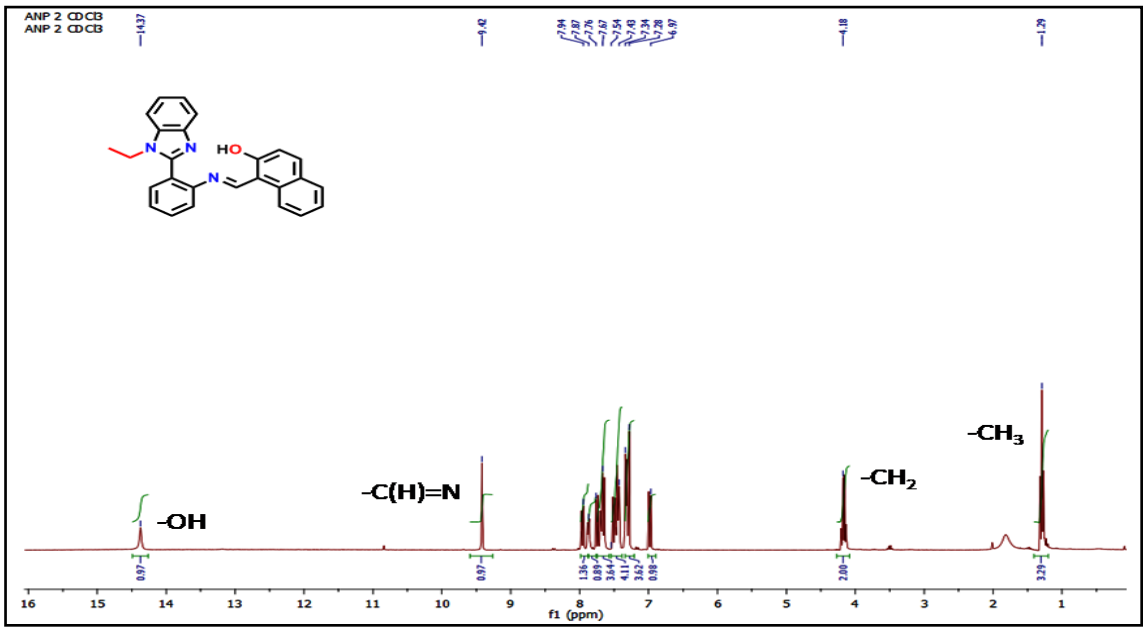


Fig. S3. ^1H NMR spectrum of **HL^2** in $CDCl_3$.

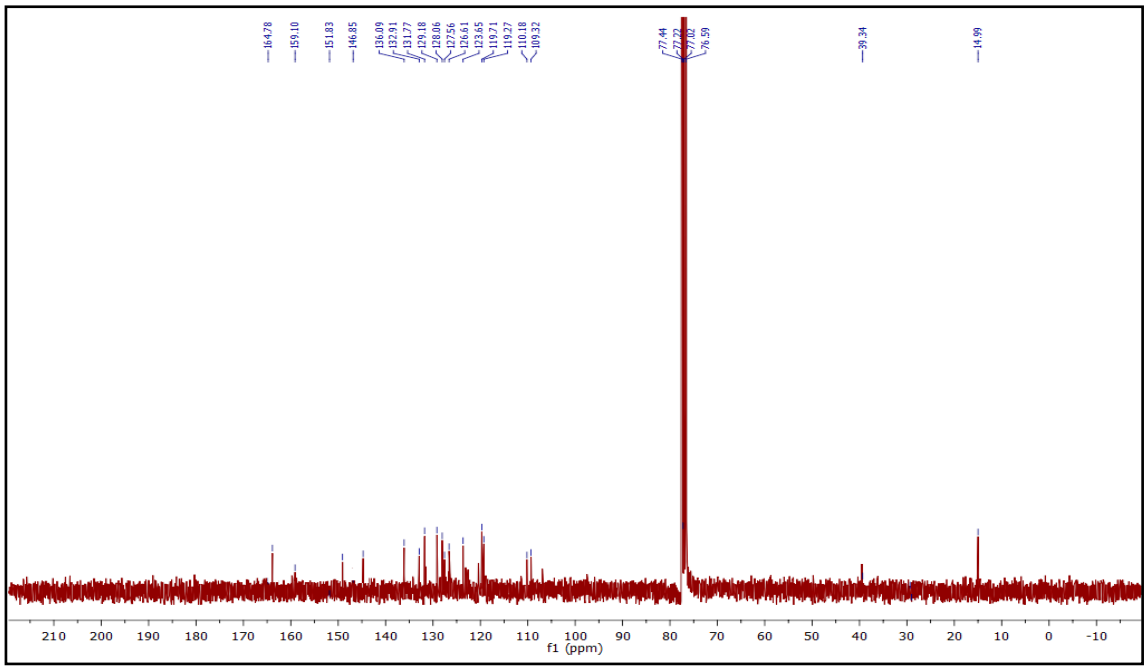


Fig. S4. ^{13}C NMR spectrum of **HL²** in $CDCl_3$.

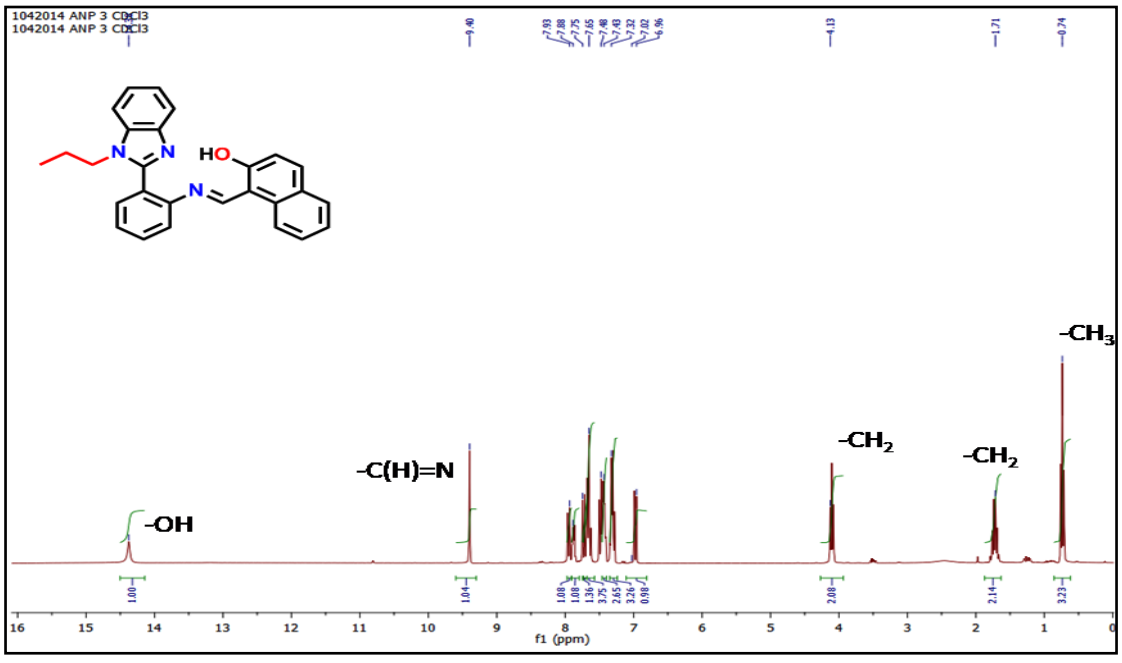


Fig. S5. ^{1}H NMR spectrum of **HL³** in $CDCl_3$.

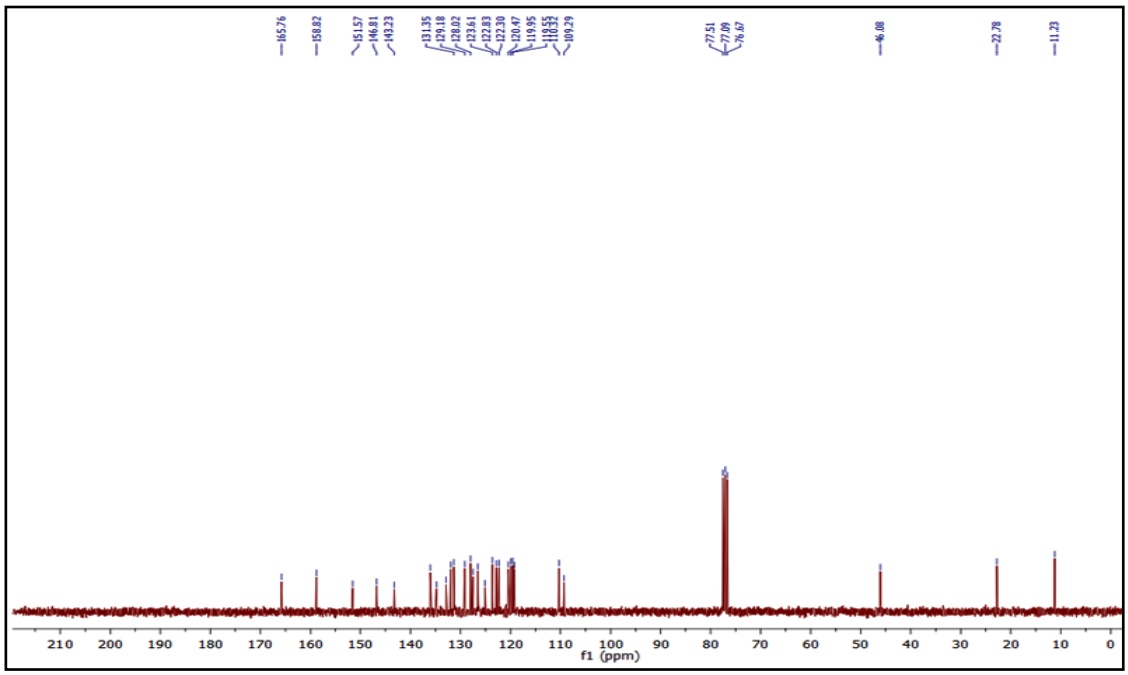


Fig. S6.^{13}CNMR spectrum of **HL^{3}** in $CDCl_3$.

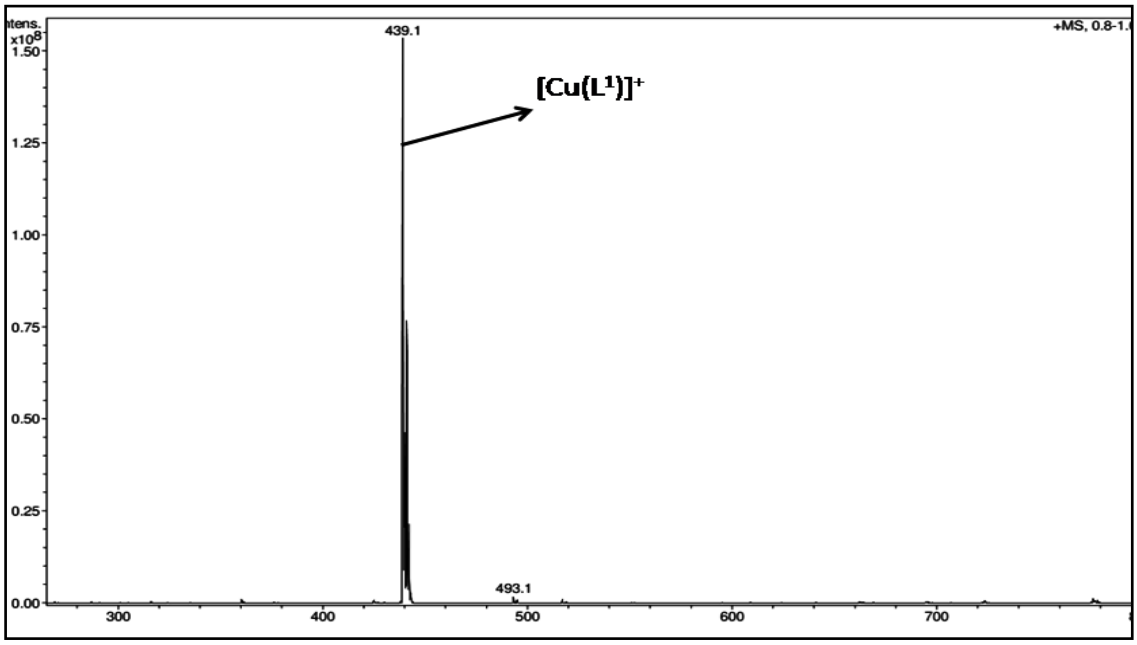


Fig. S7. ESI-MS of **1** in MeOH.

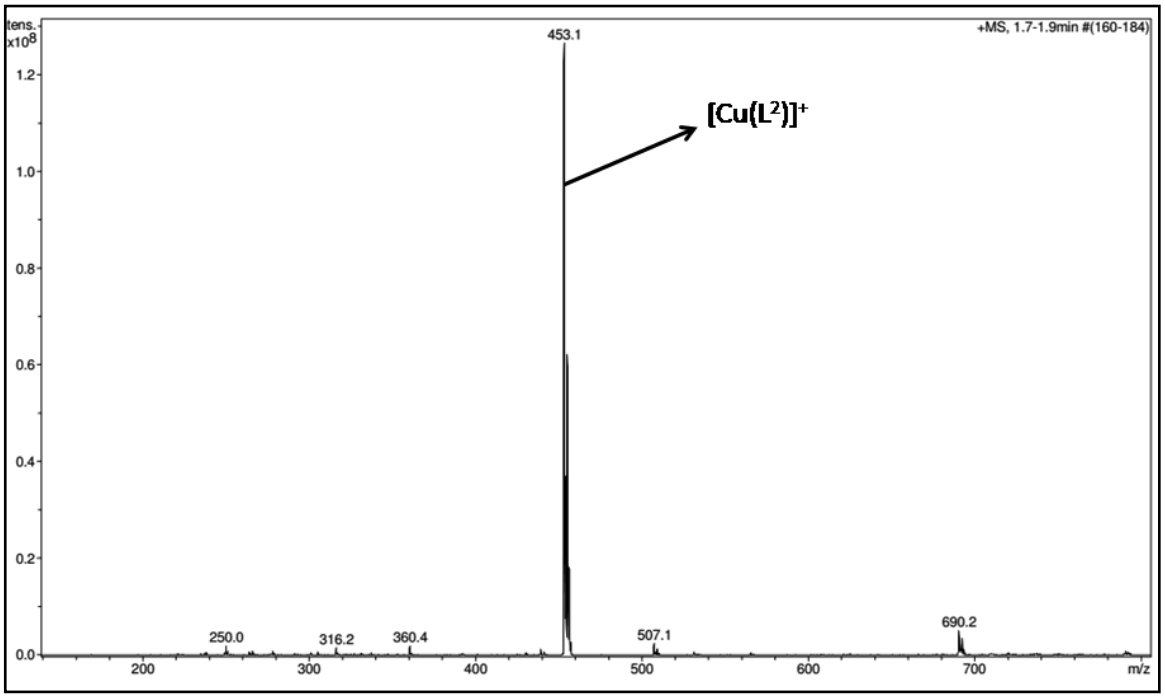


Fig. S8. ESI-MS of **2** in MeOH.

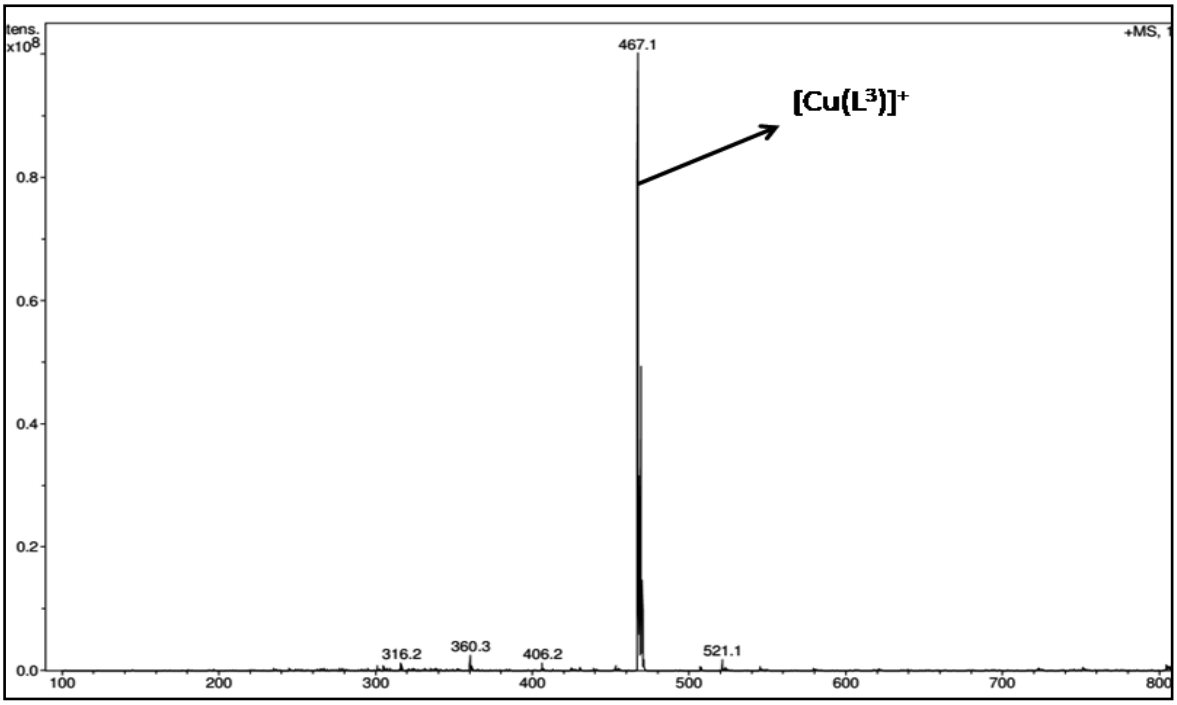


Fig. S9. ESI-MS of **3** in MeOH.

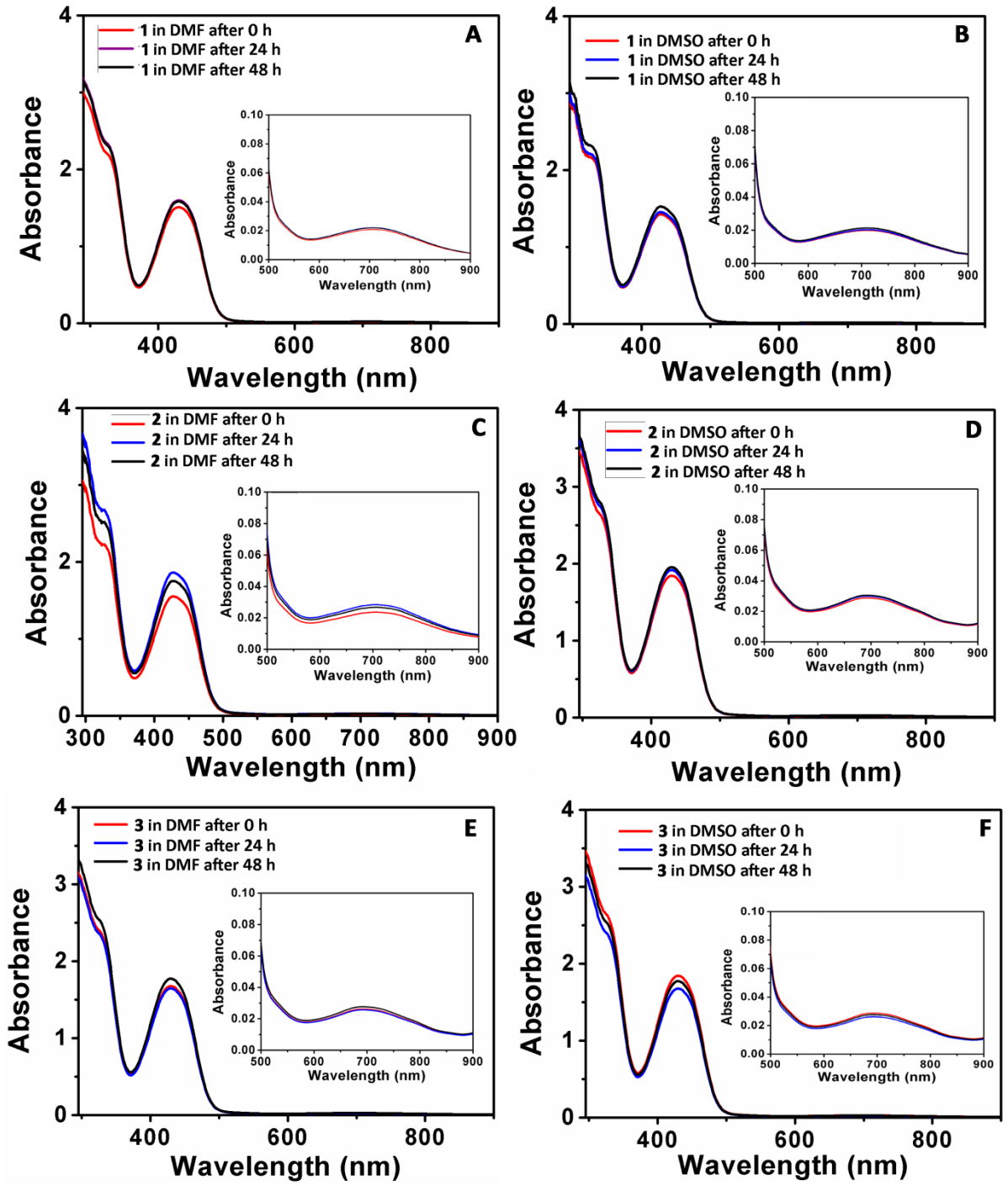


Fig. S10 UV/vis spectra recorded for **1** (A, DMF; B, DMSO; 10 μM), **2** (C, DMF; D, DMSO; 10 μM) and **3** (E, DMF; F, DMSO; 10 μM) for a fresh solution and a solution after 0, 24 and 48 h, respectively. Inset concerns the visible spectral range.

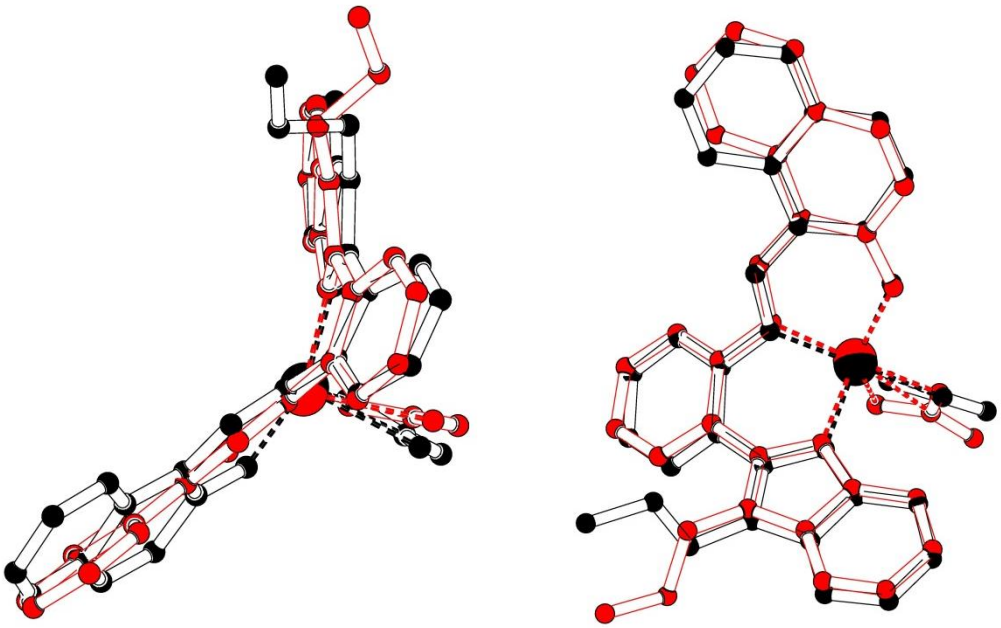


Fig. S11. Quaternion fit of the two independent copper molecules in the crystal structure of**3**(two different orientations)**.** Calculation was performed with PLATON.

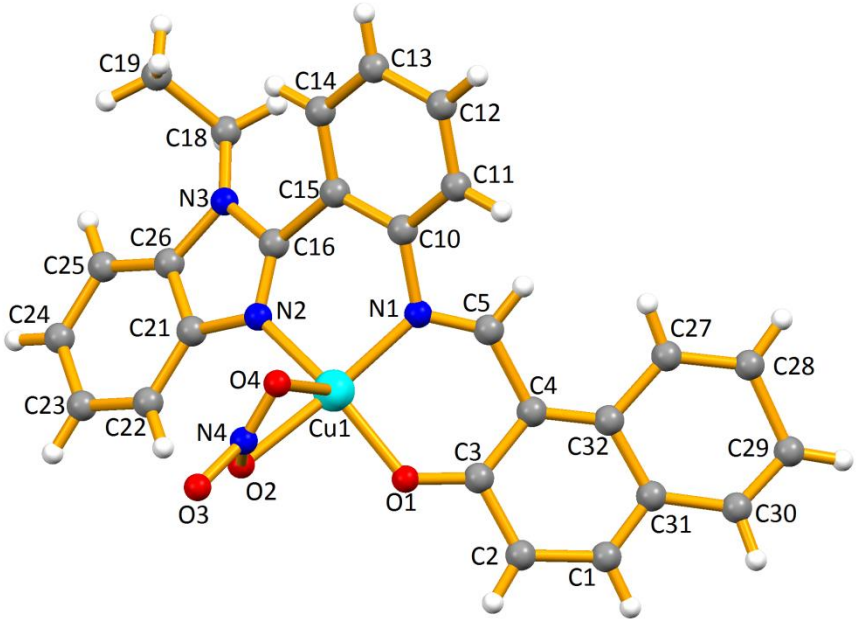


Fig. S12. X-ray molecular structure of **2** with atom numbering scheme. Space group: *P* $2_1/c$. Unit cell parameters: a = 14.913, b = 8.777 and c = 34.178 Å; β = 90.02º; V = 4473.78 $Å^3$.

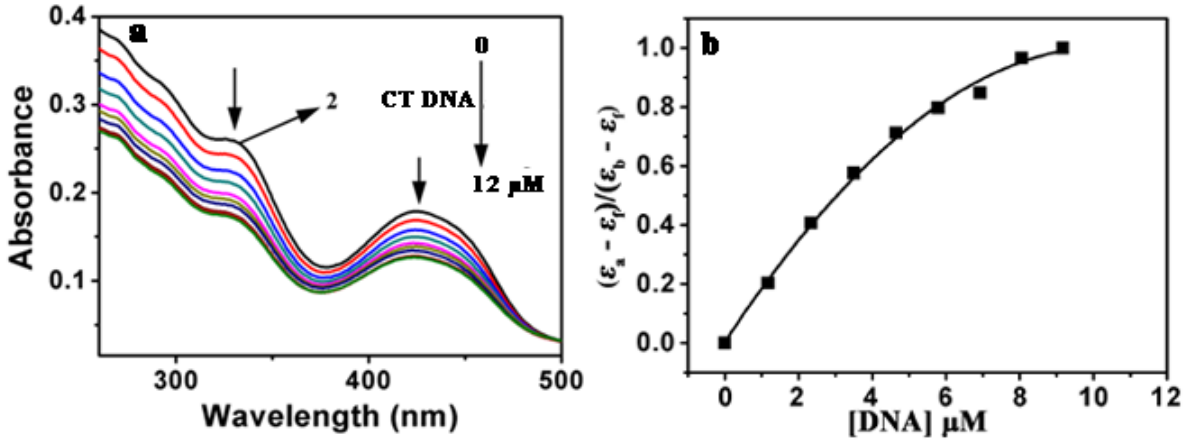


Fig. S13. (A) Absorption titration spectra of **2** in 5 mM Tris-HCl/50 mM NaCl buffer at *ca.* pH 7.5 with an increase in molar ratio of CT DNA to complex (0-12μM) at room temperature. Arrow shows the absorbance changes upon increasingCT DNA concentration. (B) Non-linear fit of the plot of $(\varepsilon_a - \varepsilon_f)/(\varepsilon_b - \varepsilon_f)$ *vs.* [DNA].

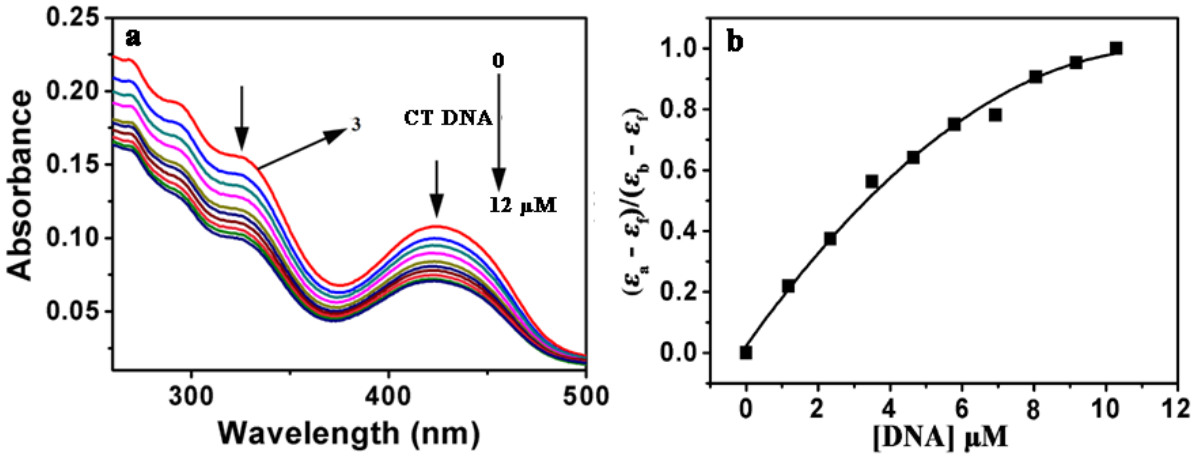


Fig. S14. (A) Absorption titration spectra of **3** in 5 mM Tris-HCl/50 mM NaCl buffer at *ca.* pH 7.5 with an increase in molar ratio of CT DNA to complex (0-12μM) at room temperature. Arrow shows the absorbance changes upon increasingCT DNA concentration. (B) Non-linear fit of the plot of $(\varepsilon_a - \varepsilon_f)/(\varepsilon_b - \varepsilon_f)$ *vs.* [DNA].

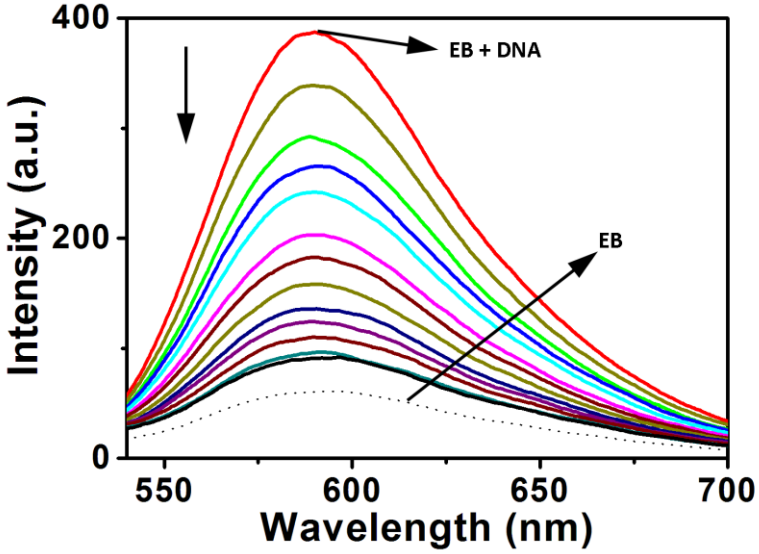


Fig. S15. Emission spectra from EB bound to the DNA in the absence (---) and in the presence of **2**. [EB] = 3.3 µM, [DNA] = 3.3 μM, [**2**] = 0-30μM.

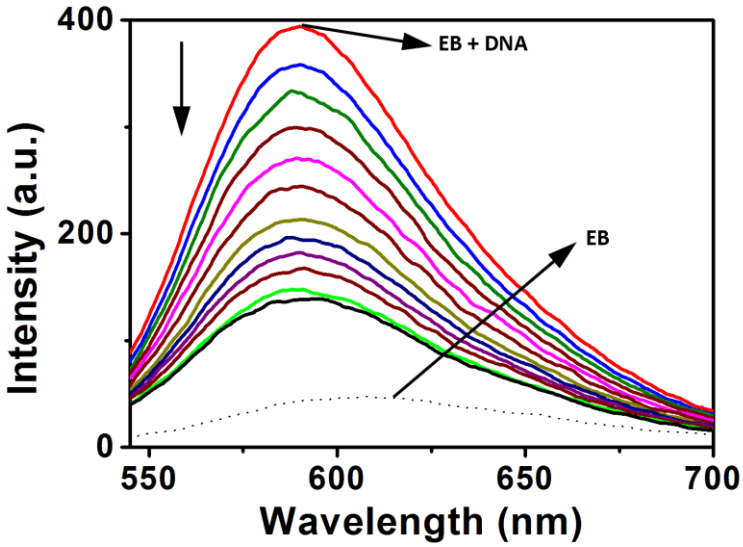
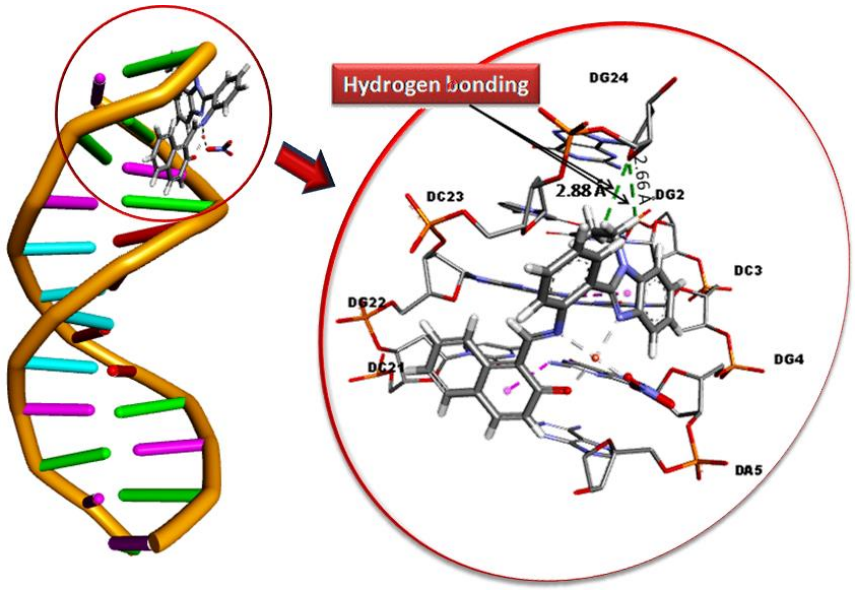
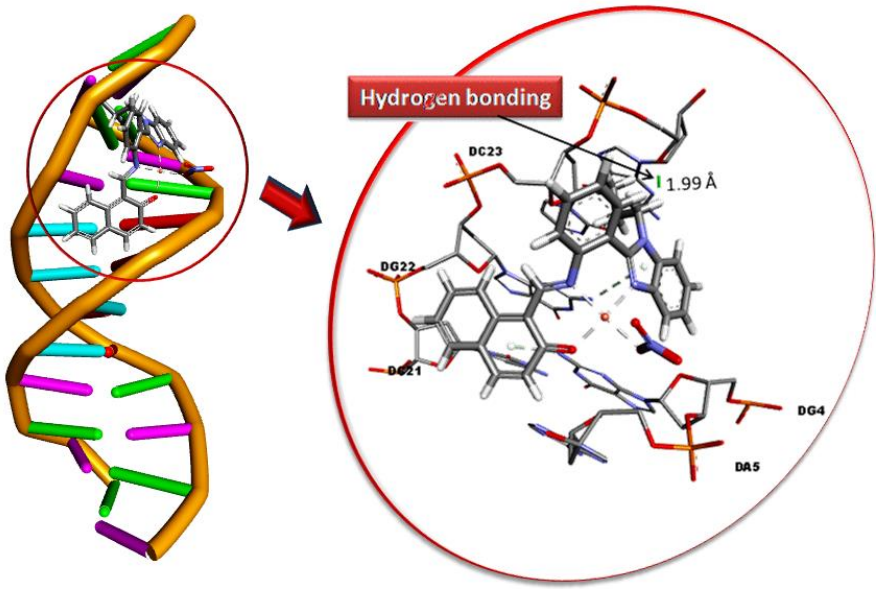


Fig. S16. Emission spectra from EB bound to the DNA in the absence (---) and in the presence of **3**. [EB] = 3.3 µM, [DNA] = 3.3 μM, [**3**] = 0-30μM.



(a) **(b)**

Fig. S17. Molecular docked model of compound **2** with DNA (PDB ID: 1BNA). DG:Guanine, DC: Cytosine, DA: Adenine.



(a) **(b)**

Fig. S18. Molecular docked model of compound **3** with DNA (PDB ID: 1BNA). DG:Guanine, DC: Cytosine, DA: Adenine.

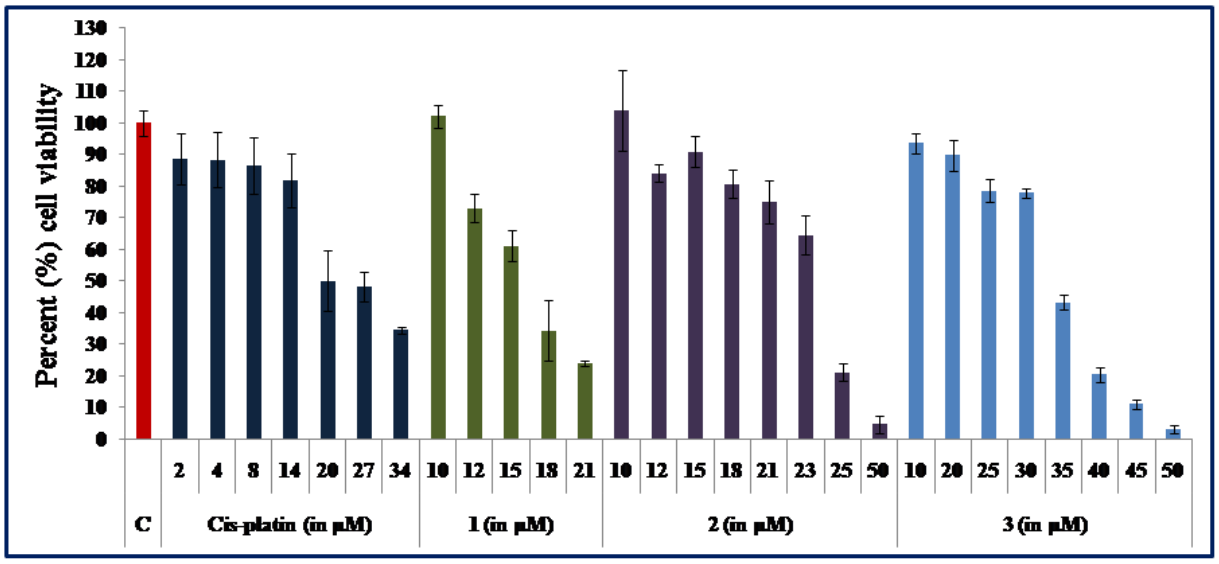


Fig. S19. MTT assay for complexes **1-3** on human lung (A-549) cancer cells. Cell viability is studied in comparison with cisplatin. Bars represent ± SD ($p < 0.05$, $n = 4$).

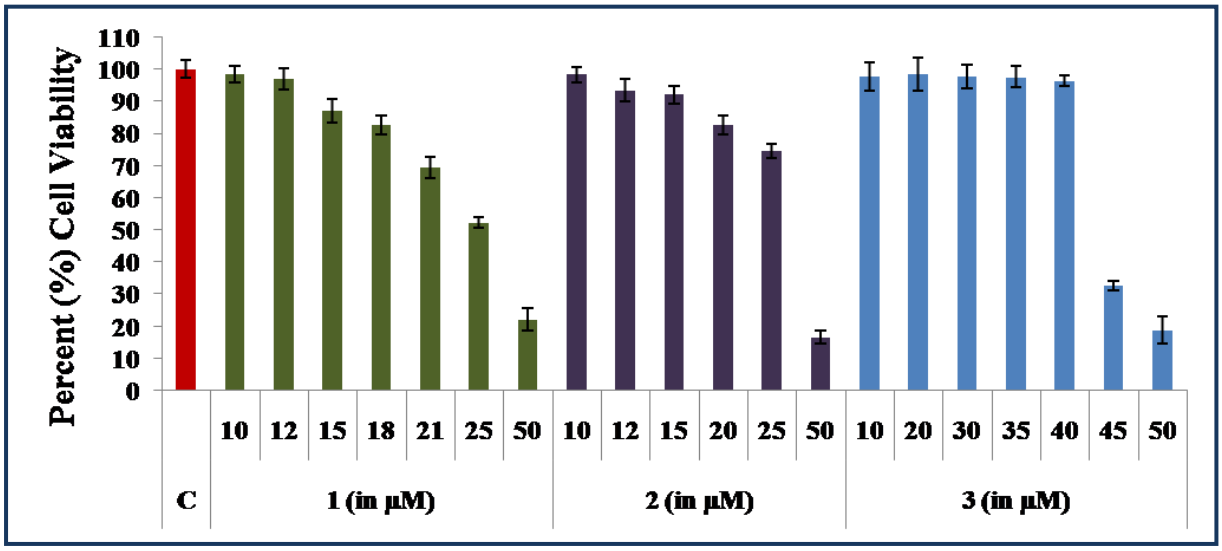


Fig. S20. MTT assay for complexes **1-3** on MDA-MB-231 cancer cells. Bars represent ± SD ($p < 0.05$, $n = 4$).

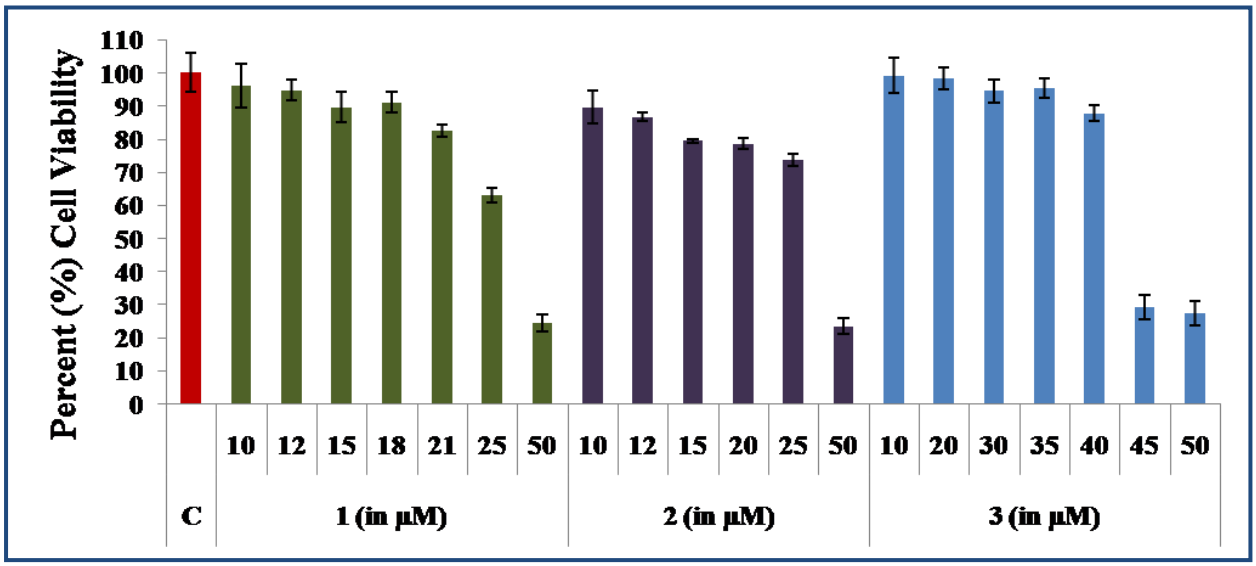


Fig. S21. MTT assay for complexes **1-3** on HeLa cancer cells. Bars represent ± SD ($p < 0.05$, $n = 4$).

Table S1. Selected experimental and calculated bond lengths (Å) of complexes **1**–**3**.

	1		**2**	**3**		
Bond length	Exp.	Theor.	Theor.	Bond length	Exp.	Theor.
Cu–N(1)	1.939	2.042	2.045	Cu–N(1)	1.973	2.045
Cu–N(3)	1.944	2.006	2.007	Cu–N(3)	1.962	2.007
Cu-O(1)	1.869	1.932	1.931	Cu-O(1)	1.862	1.933
Cu-O(2)	2.433	2.298	2.009	Cu-O(11)	2.201	2.008
Cu-O(3)	2.023	2.011	2.301	Cu-O(13)	2.455	2.303
O(2)-N(4)	1.238	1.255	1.292	N(10)-O(11)	1.285	1.292
O(3)-N(4)	1.264	1.292	1.254	N(10)-O(13)	1.244	1.254
N(4)-O(4)	1.213	1.208	1.209	N(10)-O(12)	1.202	1.209
N(1)-C(1)	1.387	1.386	1.385	O(1)-C(1)	1.310	1.277
C(1)-C(6)	1.382	1.403	1.403	C(1)-C(2)	1.413	1.447
N(2)-C(6)	1.384	1.386	1.388	C(2)-C(3)	1.339	1.354
N(2)-C(7)	1.363	1.368	1.368	C(3)-C(4)	1.392	1.438

N(1)-C(7)	1.333	1.322	1.321	C(4)-C(5)	1.422	1.409
C(1)-C(2)	1.395	1.400	1.400	C(5)-C(6)	1.360	1.379
C(2)-C(3)	1.382	1.386	1.386	C(6)-C(7)	1.382	1.409
C(3)-C(4)	1.386	1.410	1.410	C(7)-C(8)	1.388	1.438
C(4)-C(5)	1.357	1.388	1.387	C(8)-C(9)	1.388	1.354
C(5)-C(6)	1.395	1.396	1.397	C(9)-C(10)	1.482	1.447
C(1)-C(6)	1.382	1.403	1.403	C(1)-C(10)	1.416	1.431
C(7)-C(8)	1.465	1.470	1.463	C(10)-C(11)	1.401	1.413
C(8)-C(9)	1.392	1.400	1.412	N(3)-C(11)	1.322	1.313
C(9)-C(10)	1.381	1.389	1.389	N(3)-C(12)	1.421	1.410
C(10)-C(11)	1.362	1.393	1.393	C(12)-C(13)	1.386	1.401
C(11)-C(12)	1.383	1.389	1.389	C(13)-C(14)	1.384	1.390
C(12)-C(13)	1.390	1.401	1.390	C(14)-C(15)	1.369	1.393
C(13)-N(3)	1.424	1.410	1.401	C(15)-C(16)	1.354	1.389
N(3)-C(14)	1.301	1.314	1.412	C(16)-C(17)	1.392	1.400
C(14)-C(15)	1.421	1.414	1.410	C(12)-C(17)	1.407	1.412
C(15)-C(16)	1.458	1.459	1.313	C(17)-C(18)	1.452	1.471
C(16)-C(17)	1.398	1.415	1.413	N(1)-C(18)	1.317	1.321
C(17)-C(18)	1.374	1.382	1.430	N(2)-C(18)	1.391	1.385
C(18)-C(19)	1.385	1.401	1.463	N(2)-C(20)	1.381	1.385
C(19)-C(20)	1.348	1.379	1.472	C(20)-C(21)	1.394	1.400
C(20)-C(21)	1.413	1.409	1.400	C(21)-C(22)	1.386	1.386
C(16)-C(21)	1.413	1.418	1.389	C(22)-C(23)	1.312	1.410
C(21)-C(22)	1.418	1.437	1.393	C(23)-C(24)	1.410	1.387
C(22)-C(23)	1.340	1.354	1.390	C(24)-C(25)	1.362	1.397
C(23)-C(24)	1.417	1.447	1.401	N(1)-C(25)	1.403	1.388
C(15)-C(24)	1.411	1.430	1.412	N(2)-C(26)	1.479	1.461
O(1)-C(24)	1.302	1.277	1.410	C(26)-C(27)	1.530	1.528

				C(27)-C(28)	1.522	1.526