Supporting Information

Copper(II) complexes based on quinoline derived Schiff-base ligands: Synthesis, characterization, HSA/DNA binding ability, and anticancer activity

Kun Hu*[a], Chensi Liu[a], Jingui Li[a], Fupei Liang*[a,b]

[a]State Key Laboratory Cultivation Base for Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmacy, Guangxi Normal University, 15 Yucai Road, Guilin 541004, P. R. China., Fax, 086-773-2120958 ; E-mail: fliangoffice@yahoo.com.

[b]Guangxi Key Laboratory of Electrochemical and Magnetochemical Functional Materials, College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, China.

*Corresponding authors: hukun216@163.com (Kun Hu); fliangoffice@yahoo.com (Fupei Liang).

Contents:

Table S1 Crystal data and structure refinement for complexes **C1**-**C3**.

Complex	**C1**	**C2**	**C3**
Empirical formula	$C_{18}H_{14}CuN_4O_8$	$C_{19}H_{16}Cl_2CuN_2O_2$	$C_{19}H_{16}CuN_2O_7S$
Formula weight	477.87	438.78	479.94
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*-1	$P2_1/n$	*P*-1
a (Å)	10.093(3)	9.784 (8)	8.818 (5)
b (Å)	10.384(3)	12.520 (11)	9.995 (6)
c (Å)	10.818(3)	15.403 (13)	13.151 (7)
α (°)	78.634(4)	90.00	99.756 (9)
β (°)	65.151(4)	101.907 (13)	104.779 (8)
γ (°)	71.085(4)	90.00	103.630 (8)
Volume (Å^3)	970.8(5)	1846 (3)	1056.2 (10)
Z	2	4	2
Calculated density(Mg/m^3)	1.635	1.579	1.459
F(000)	486	892	475
θ range for data collection (°)	2.1-26.5	2.1-26.5	1.7-25.4
Reflections collected/unique	11785/4023	21771/3793	8547/3853
Goodness-of-fit on F^2	1.045	1.047	1.057
R_{int}	0.025	0.036	0.047
Final *R* indices [$I > 2\sigma(I)$]	0.0332	0.0254	0.0680
R indices (all data)	0.0414	0.0321	0.0910

Table S2 Selected bond lengths (Å) and bond angles (°) for complexes **C1-C3**.

C1			
Cu1−O5	2.0128(18)	Cu1−N1	1.984(2)
Cu1−O6	1.9820(19)	Cu1−N2	1.9448(19)
O6−Cu1−O8	57.05(7)	N2−Cu1−O5	159.13(8)
O5−Cu1−O6	85.01(9)	N2−Cu1−O8	110.91(10)
O5−Cu1−O8	85.44(10)	N2−Cu1−N1	94.96(8)
O5−Cu1−N1	94.89(8)	N1−Cu1−O6	156.73(8)
N2−Cu1−O6	93.05(8)	N1−Cu1−O8	99.71(8)
C2			
Cu1−Cl1	2.2272 (19)	Cu1−N1	1.987 (2)
Cu1−Cl2	2.2255 (15)	Cu1−N2	1.9855 (19)
Cl2−Cu1−Cl1	101.64 (3)	N2−Cu1−Cl1	133.52 (5)
N1−Cu1−Cl1	100.30 (6)	N2−Cu1−Cl2	96.67 (7)
N1−Cu1−Cl2	138.00 (6)	N2−Cu1−N1	93.51 (7)
C3 (Symmetry code: (i) $-x + 1, -y + 2, -z + 2$.)			
Cu1−O1	2.009 (4)	Cu1−O4i	2.223 (4)
Cu1−O2	1.989 (4)	Cu1−N1	1.958 (5)
Cu1−N2	1.979 (5)	N1−Cu1−O2	96.09 (17)
O1−Cu1−O4i	99.69 (16)	N1−Cu1−O4i	97.82 (17)
O2−Cu1−O1	70.86 (16)	N1−Cu1−N2	94.9 (2)
O2−Cu1−O4i	104.74 (17)	N2−Cu1−O1	93.77 (18)
N1−Cu1−O1	160.35 (18)	N2−Cu1−O2	159.58 (19)
N2−Cu1−O4i	90.75 (19)	N1−Cu1−O2	96.09 (17)

Fig. S1 FT-IR (KBr) spectra of ligand L1.

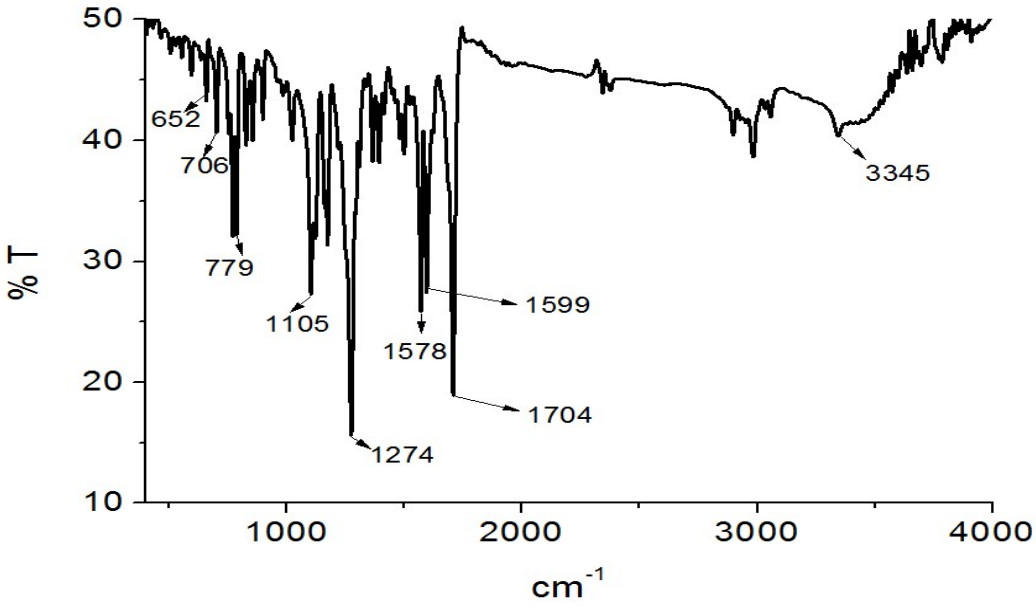


Fig. S2 The HRMS (ESI) spectra of ligand L1 in the methanol solution.

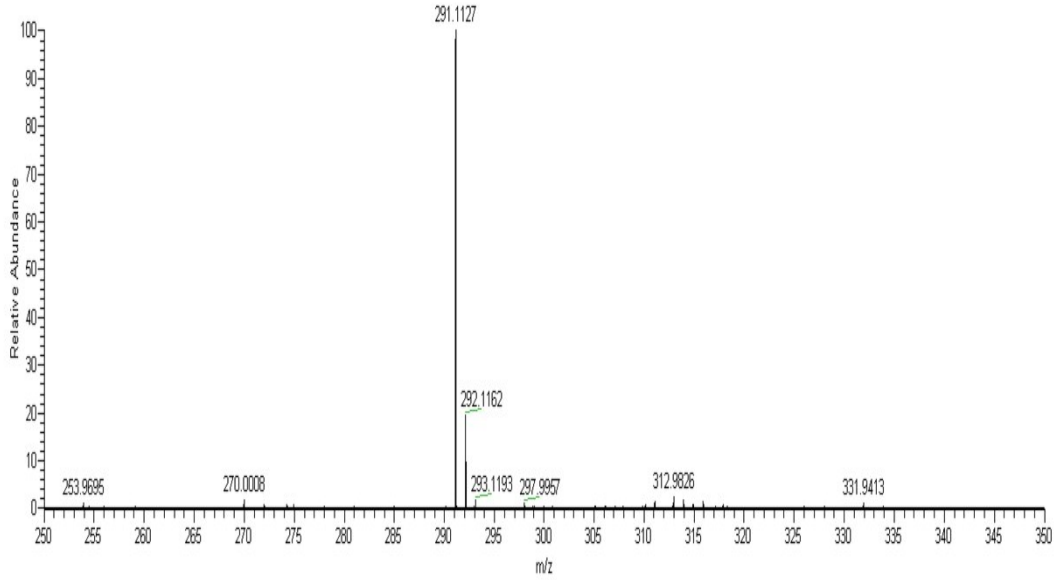


Fig. S3 ^{1}H NMR spectra of ligand L1 in DMSO.

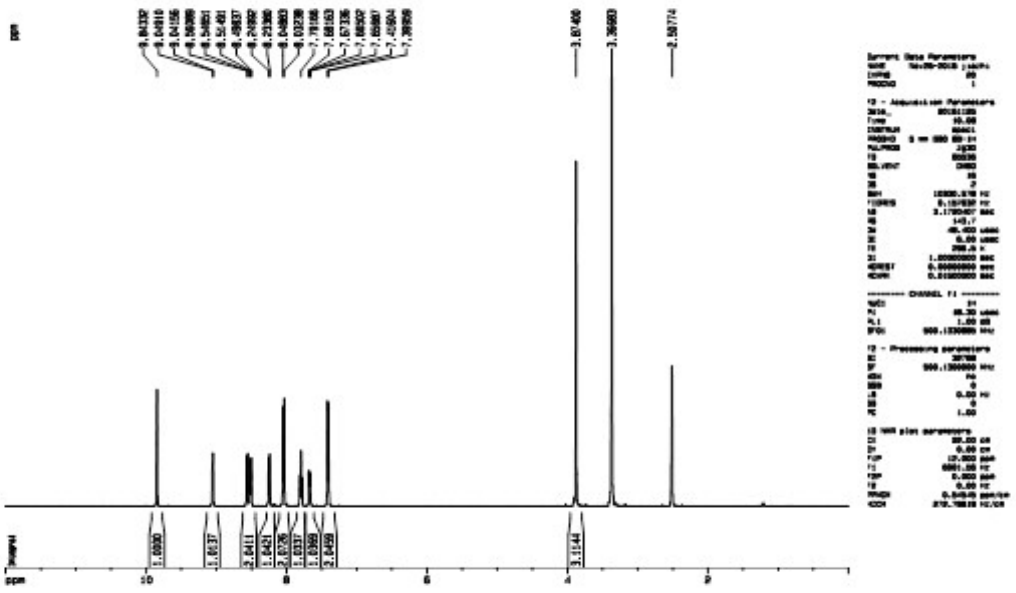


Fig. S4 FT-IR (KBr) spectra of ligand L2.

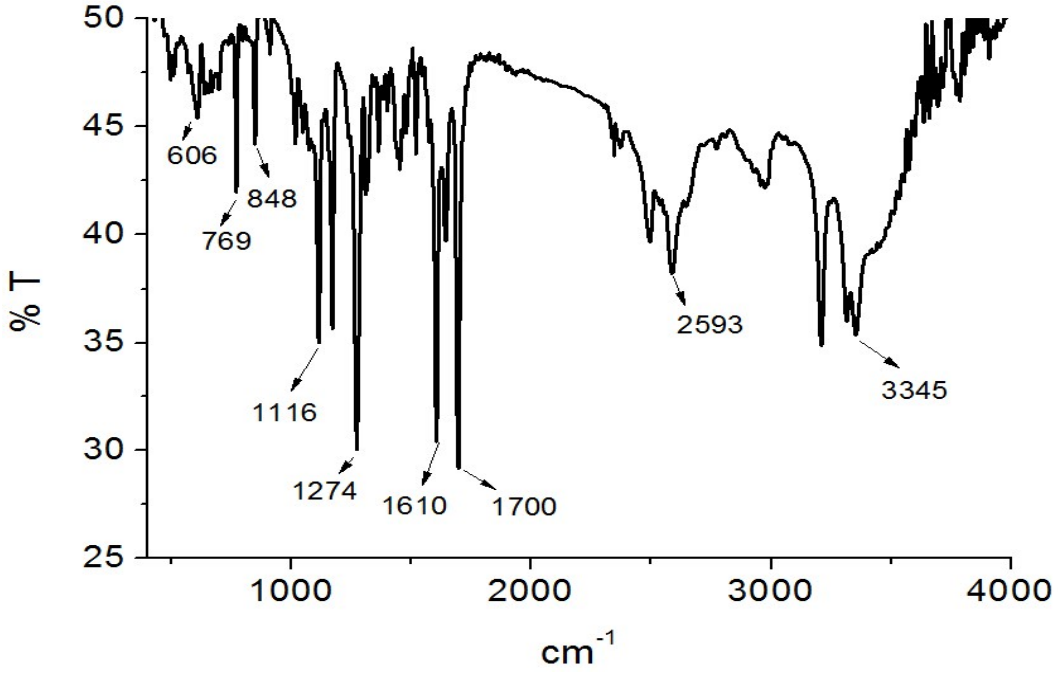


Fig. S5 The HRMS (ESI) spectra of ligand L2 in the methanol solution.

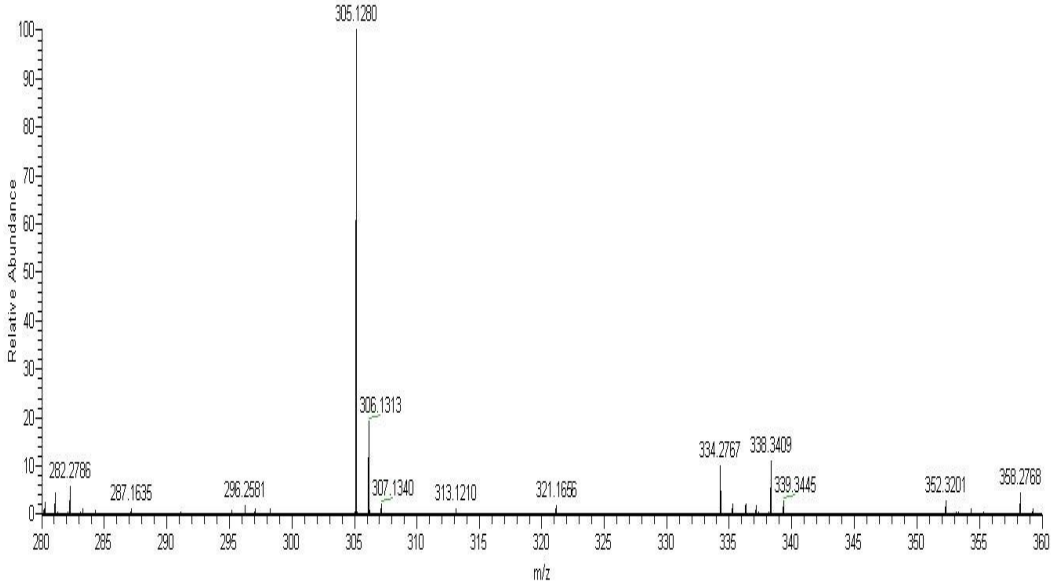


Fig. S6 ^{1}H NMR spectra of ligand L2 in DMSO.

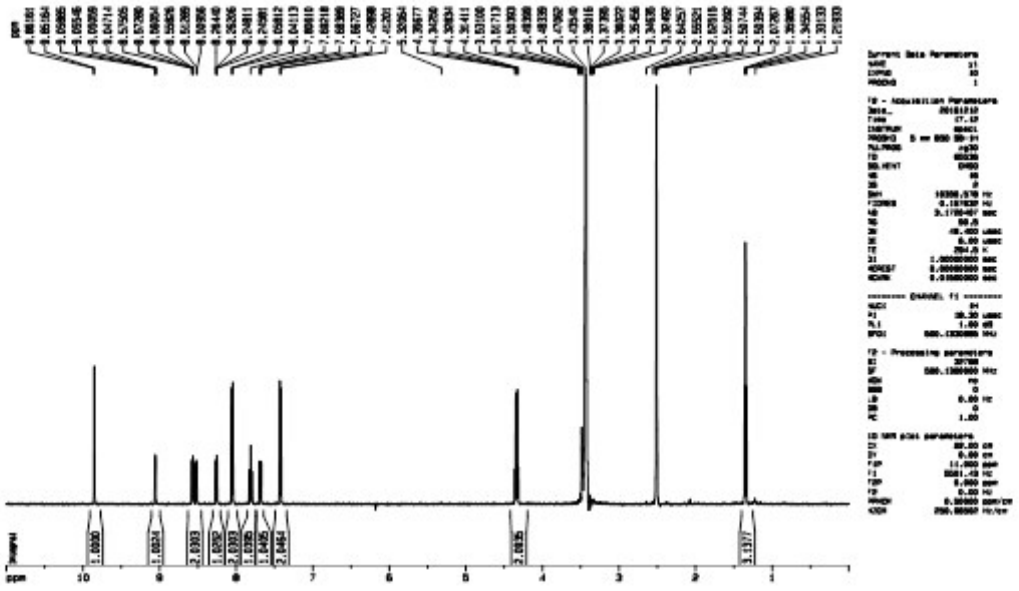


Fig. S7 FT-IR (KBr) spectra of complex **C1**.

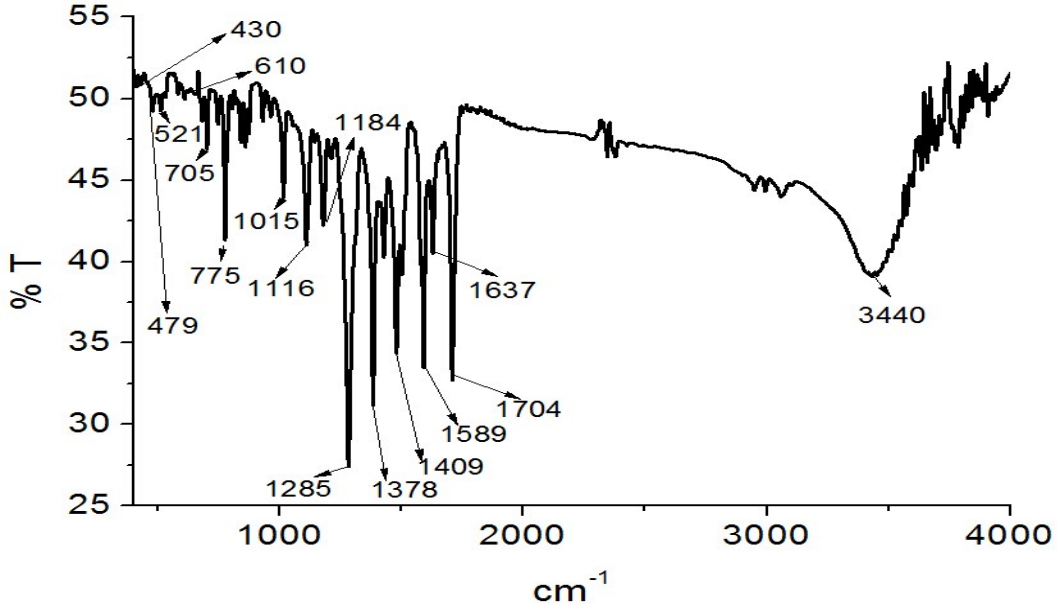


Fig. S8 The HRMS (ESI) spectra of complex **C1** in the methanol solution.

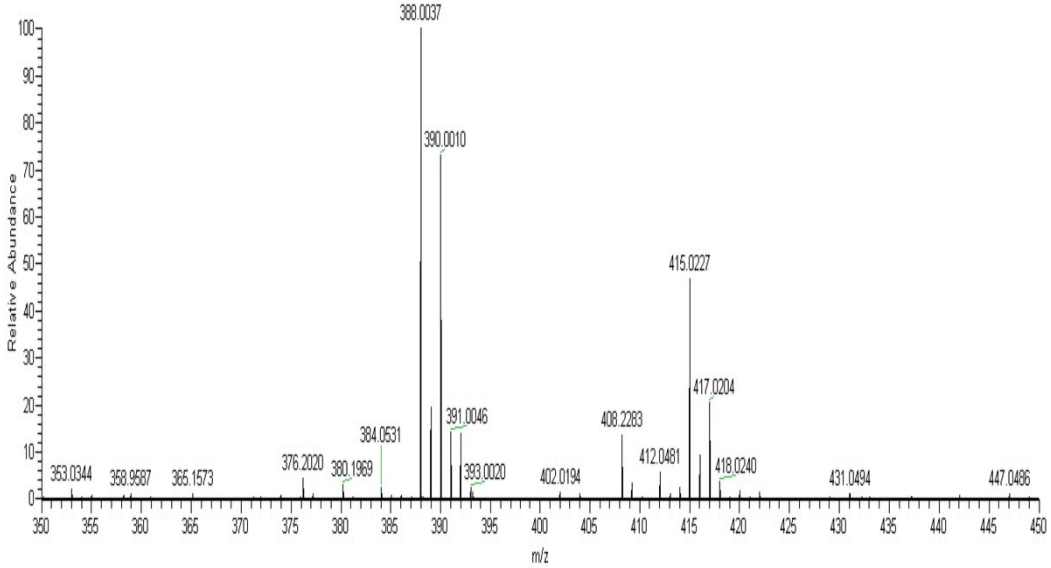


Fig. S9 FT-IR (KBr) spectra of complex **C2**.

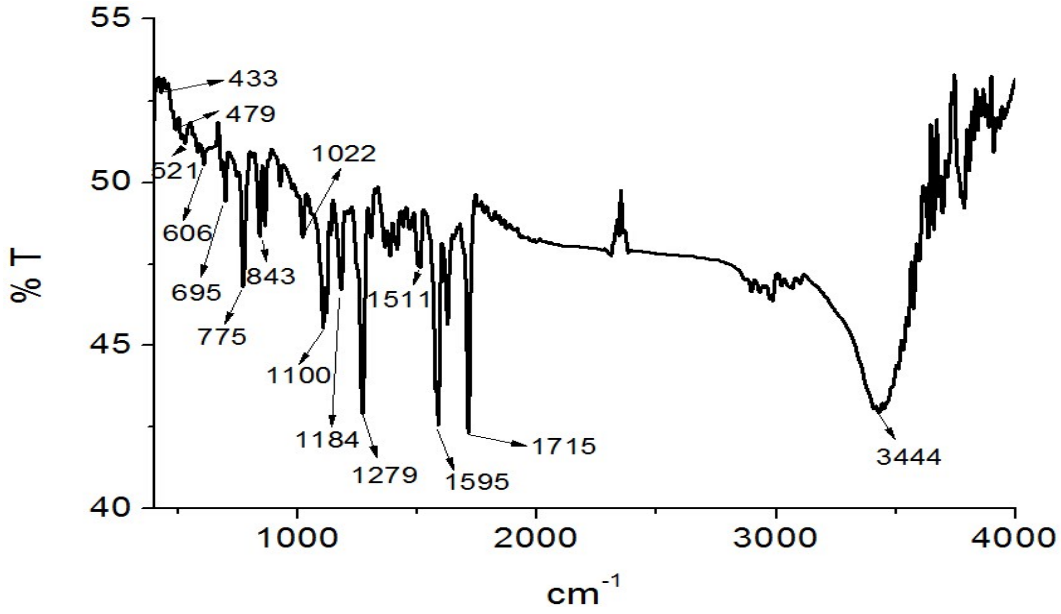


Fig. S10 The HRMS (ESI) spectra of complex **C2** in the methanol solution.

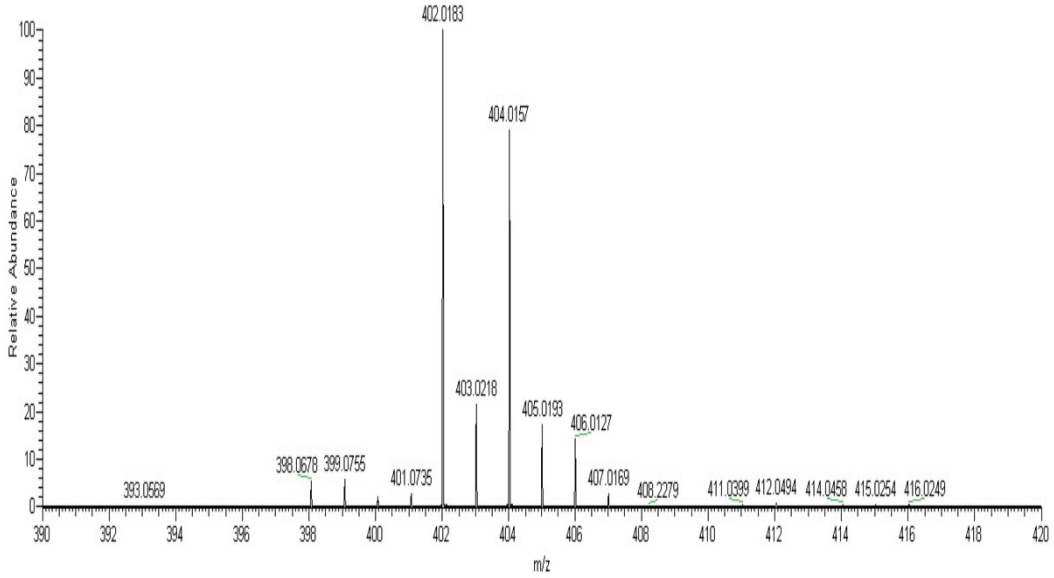


Fig.S11 FT-IR (KBr) spectra of complex **C3**.

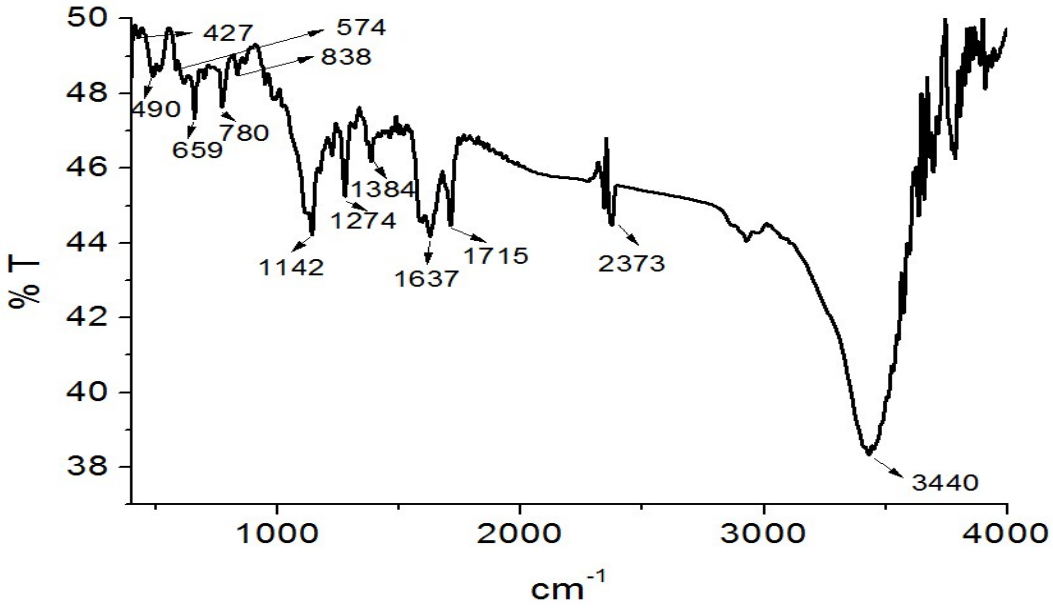


Fig. S12 The HRMS (ESI) spectra of complex **C3** in the methanol solution.

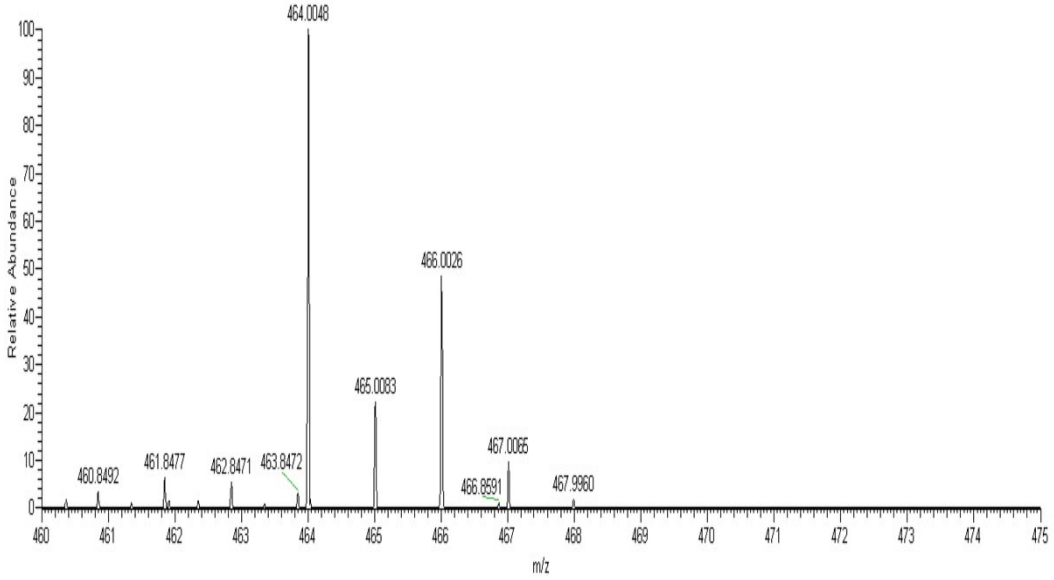
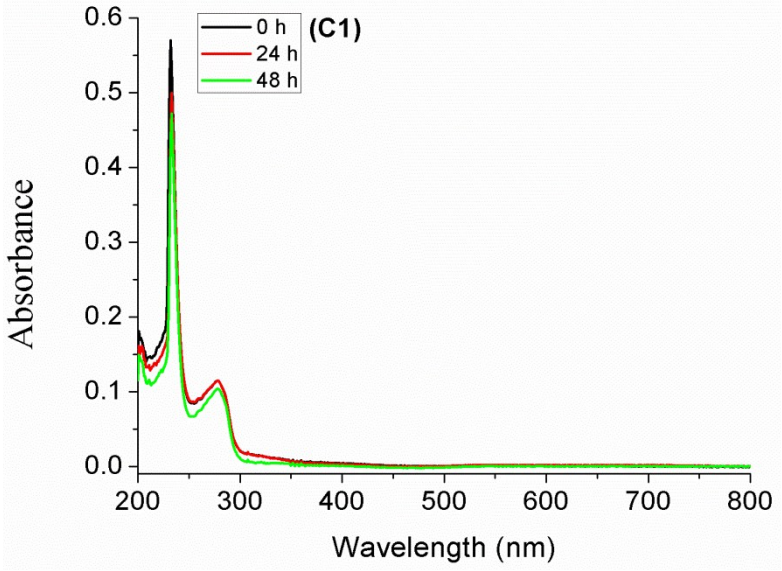
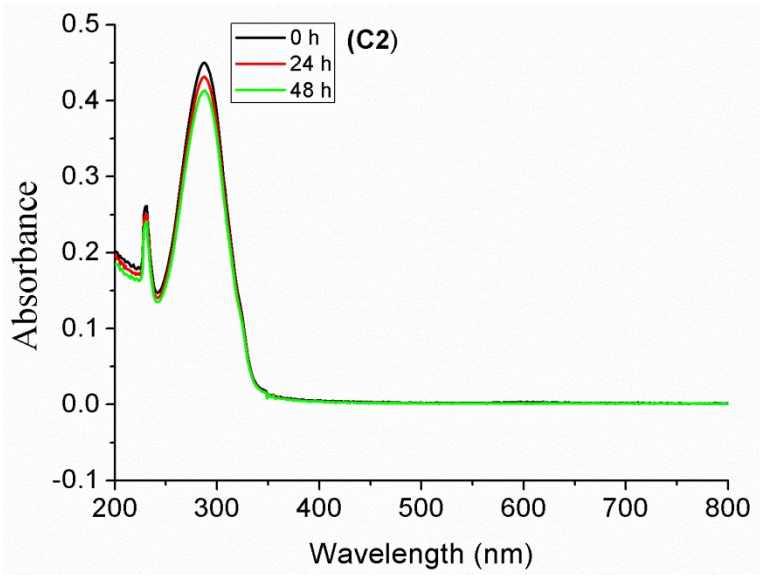


Fig. S13 UV-Vis absorption spectra of complex **C1-C3** (1.0×10^{-6} M) in Tris-HCl buffer solution (0.1% DMSO) in the time course 0 and 48 h, respectively.





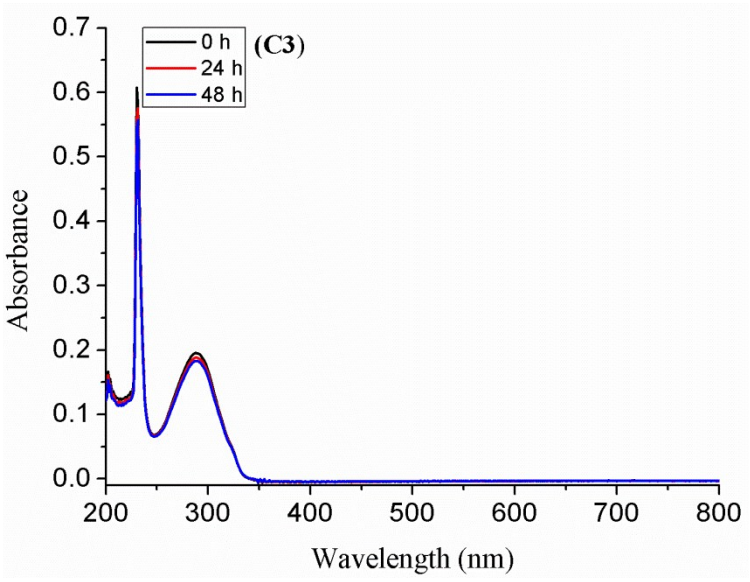

0 h
24 h
48 h
(C3)
Absorbance
Wavelength (nm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
200
300
400
500
600
700
800

Fig. S14 Emission spectra of HSA (1μM; λex=280 nm) in the presence increasing concentrations of the ligand L1 (A) and L2 (B) (0, 1.0, 2.0, 3.0, 4.0 and 5.0 μM).

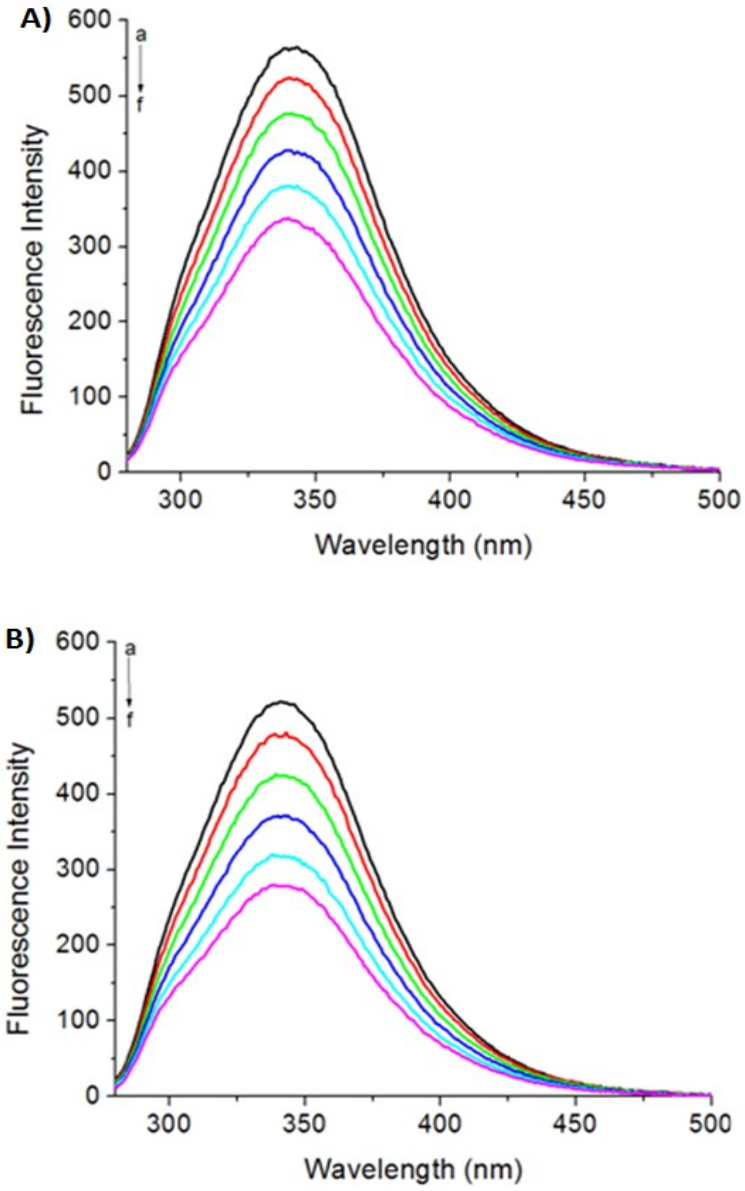


Fig.S15 Stern-Volmer (A) and (B) Hill plots for HSA interacting with the test compounds at 295 K. Conditions: HSA= 1.0 μM; complexes: 0, 1.0, 2.0, 3.0, 4.0 and 5.0 μM.

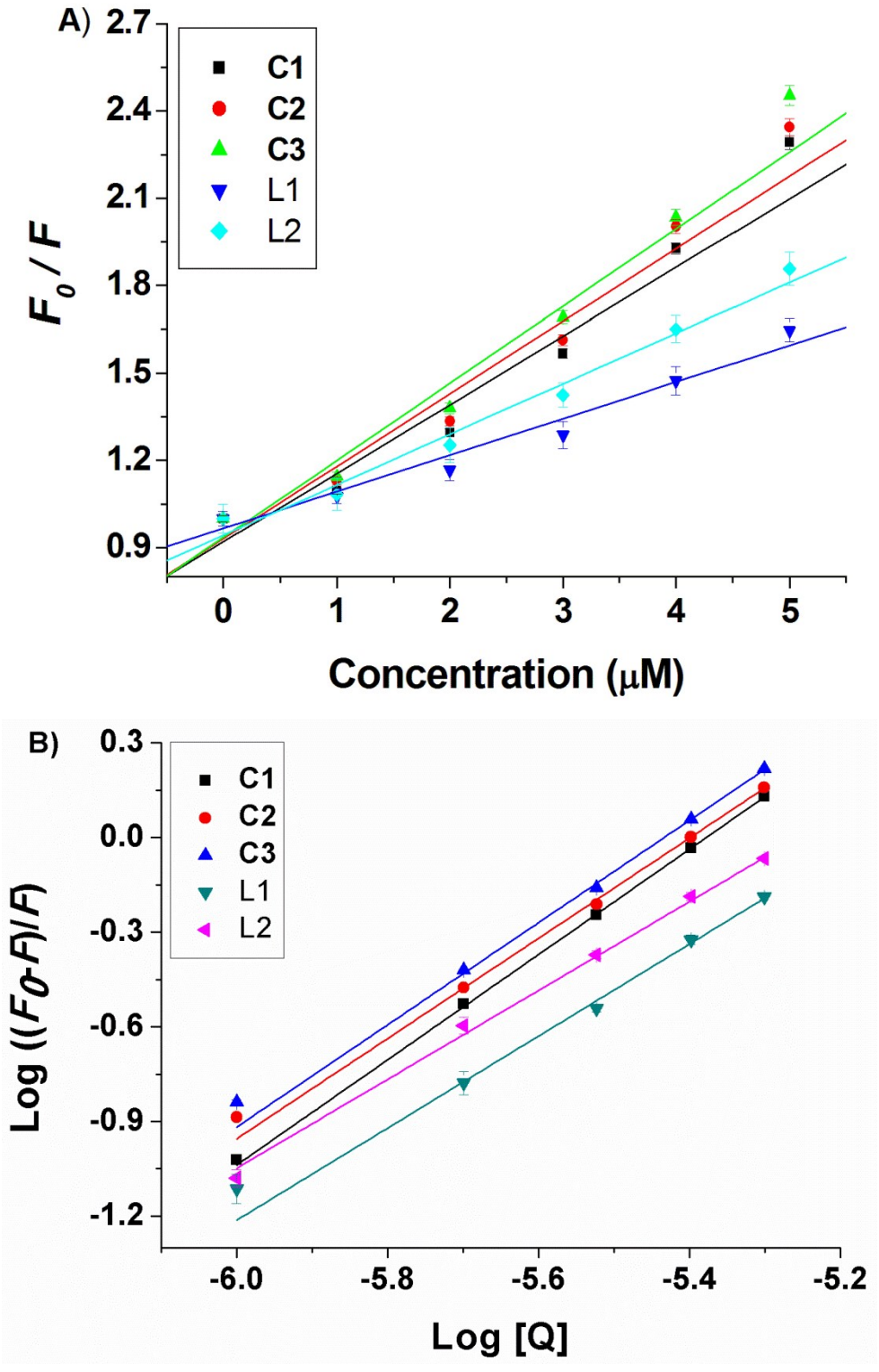


Fig. S16 UV-Vis absorption spectra of HSA (2.5 μM) in the presence of ligand L2 and complex **C3** (2.5 μM).

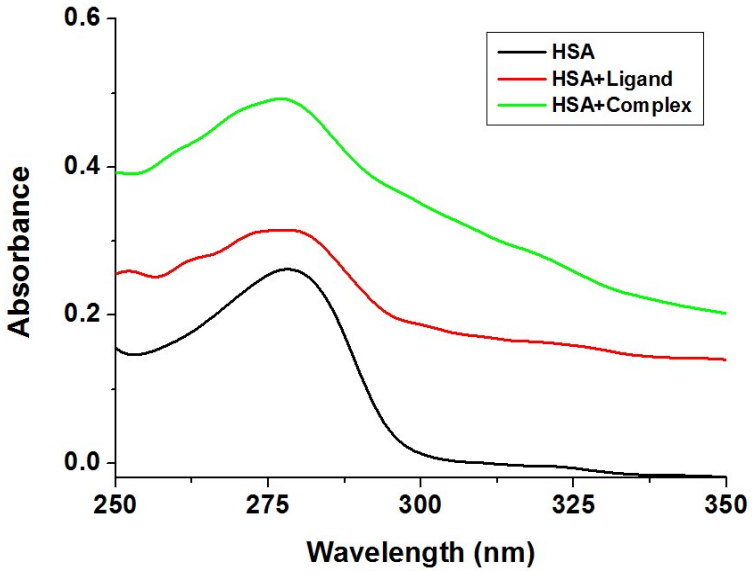
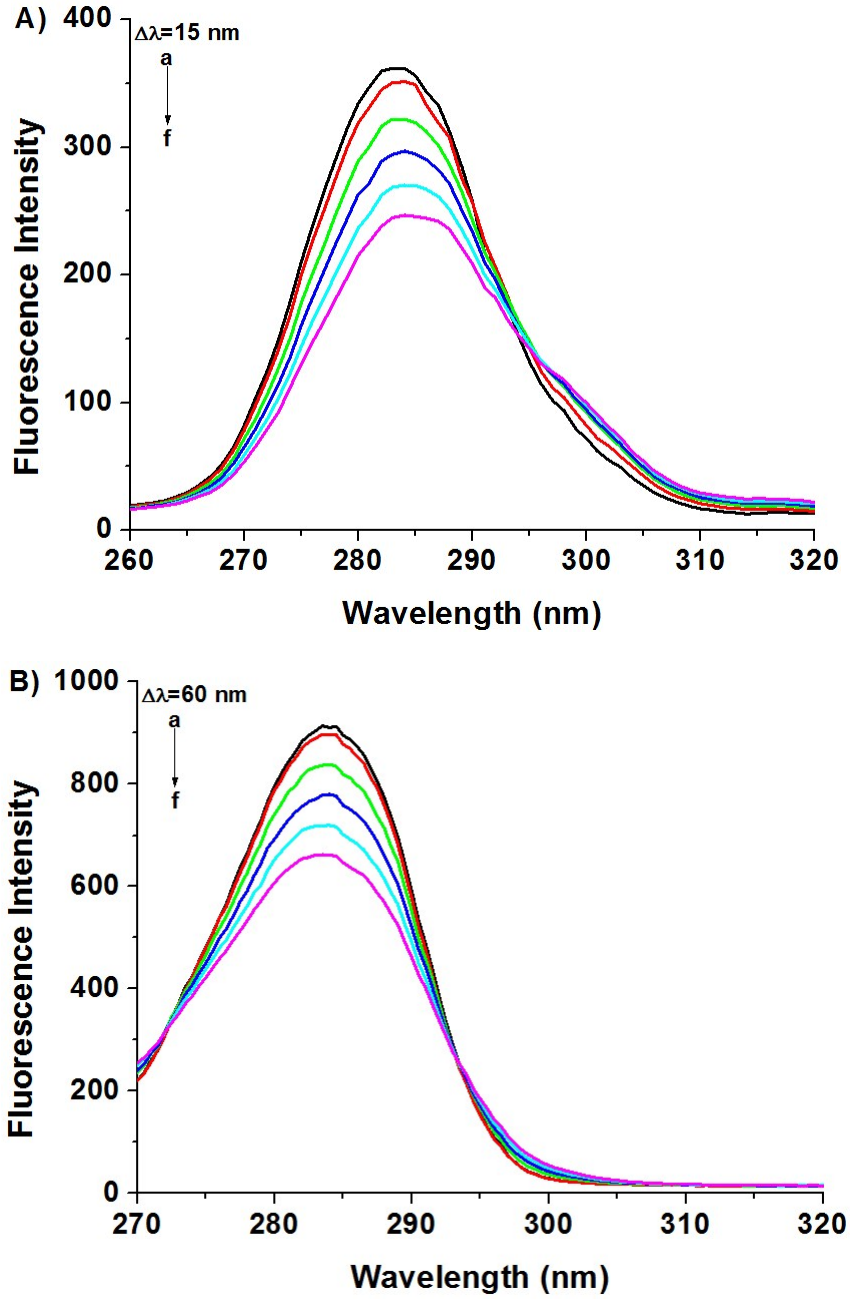
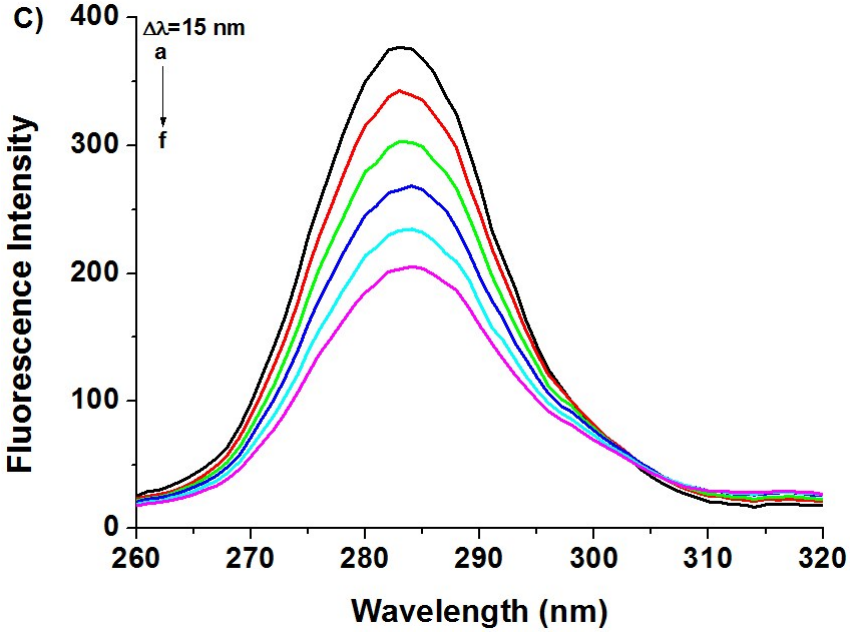
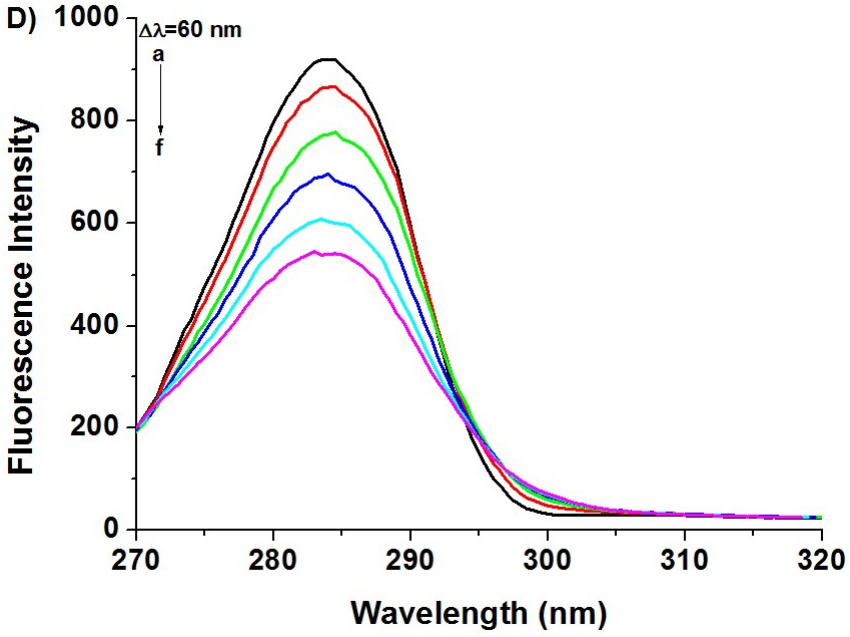
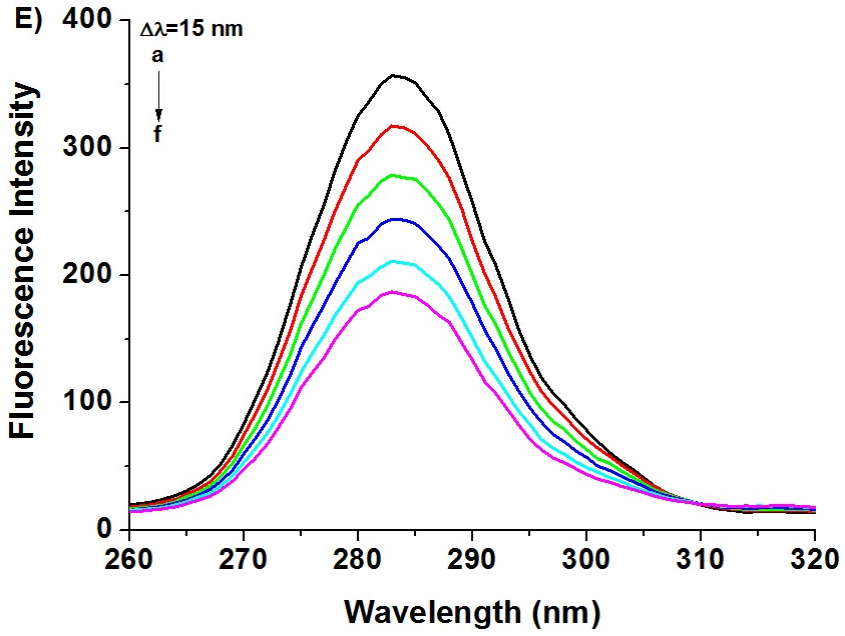


Fig. S17 Synchronous fluorescence spectra of HSA (1.0 μM, black line) in presence of increasing amounts of complex **C1** (A, B), **C2** (C, D) and **C3** (E, F) (0-5.0 μM) with a wavelength difference of Δλ=15 nm (A, **C1**; C, **C2**, and E, **C3**) and Δλ=60 nm (B, **C1**; D, **C2**, and F, **C3**).




C)
Δλ=15 nm
a
f
Fluorescence Intensity
0
100
200
300
400
260
270
280
290
300
310
320
Wavelength (nm)


D)
Δλ=60 nm
a
f
Fluorescence Intensity
0
200
400
600
800
1000
270
280
290
300
310
320
Wavelength (nm)


E)
Δλ=15 nm
a
f
Fluorescence Intensity
0
100
200
300
400
260
270
280
290
300
310
320
Wavelength (nm)

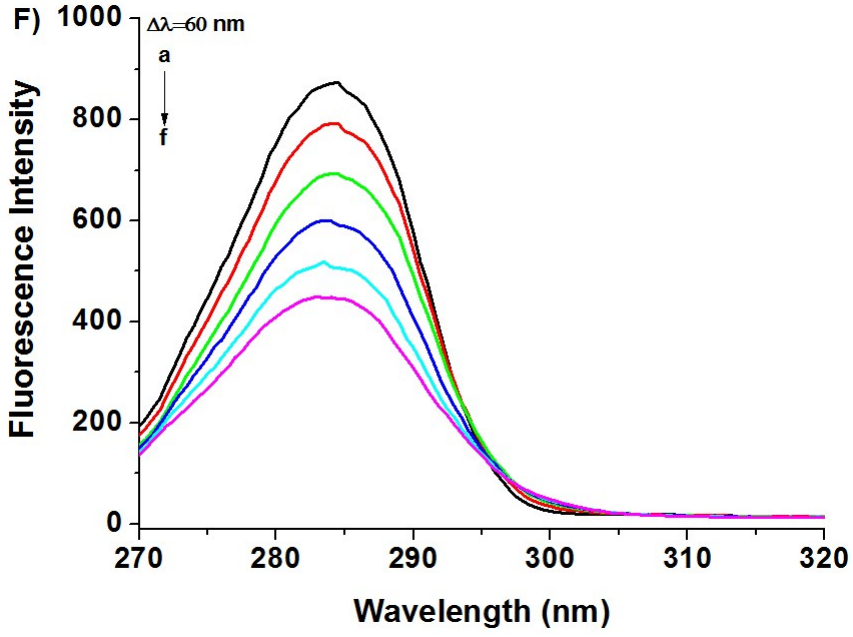

F)
Δλ=60 nm
a
f
Fluorescence Intensity
0
200
400
600
800
1000
270
280
290
300
310
320
Wavelength (nm)

Fig. S18 The high-performance liquid chromatographic (HPLC) spectra of HSA and HSA-**C3** mixture. Condition: HSA 2.5 μM; **C3,** L2 2.5 μM; Separation was carried out on a Sinochrom ODS-AP column (150 mm × 4.6 mm id, 300 Å pore size, 5 μm particle sizes; Elite, Dalian, China). The absorbance of the effluent was detected at 280 nm. The flow rate was set to 0.5 mL/min with isocratic elution. Mobile phase A: ACN containing 0.1% formic acid; mobile phase B: water containing 0.1% formic acid.

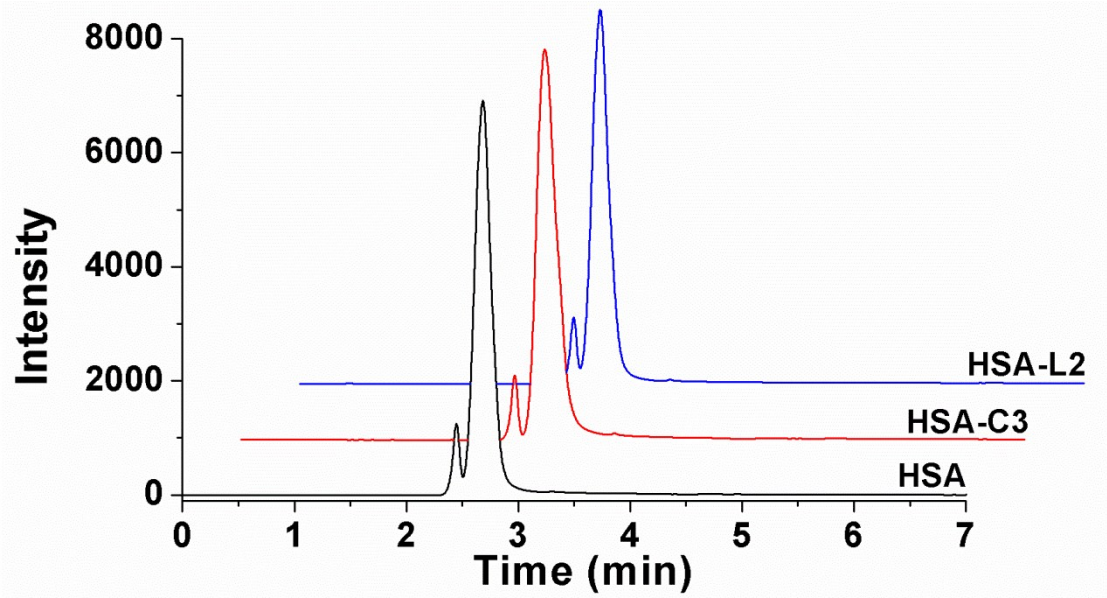
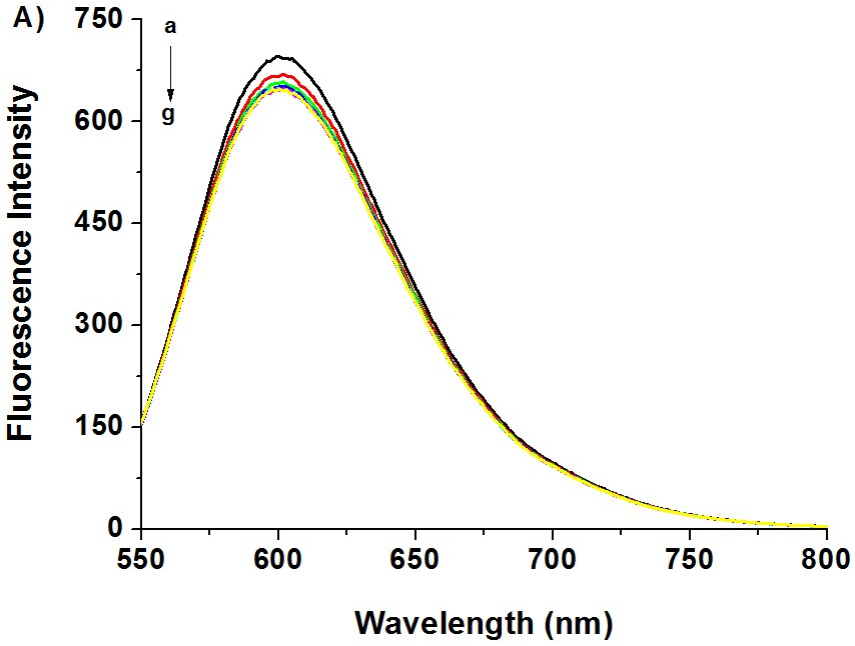


Fig. S19 Fluorescence quenching spectra of DNA-EB (10 μM) in the presence of ligand L1 (A) and L2 (B) (0-30 μM).



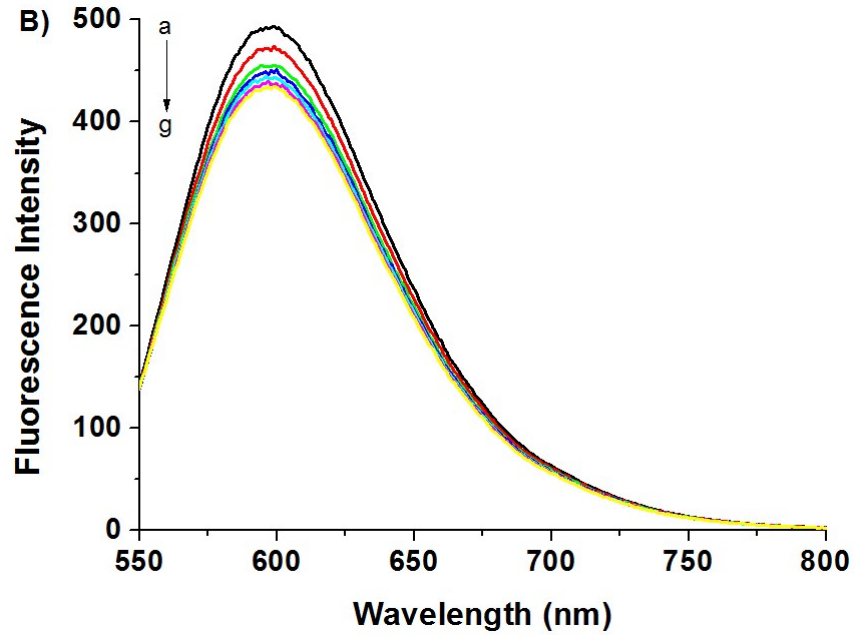


Fig. S20 Stern-Volmer plots of the fluorescence titrations of the ligand and the complex (0-30 μM).

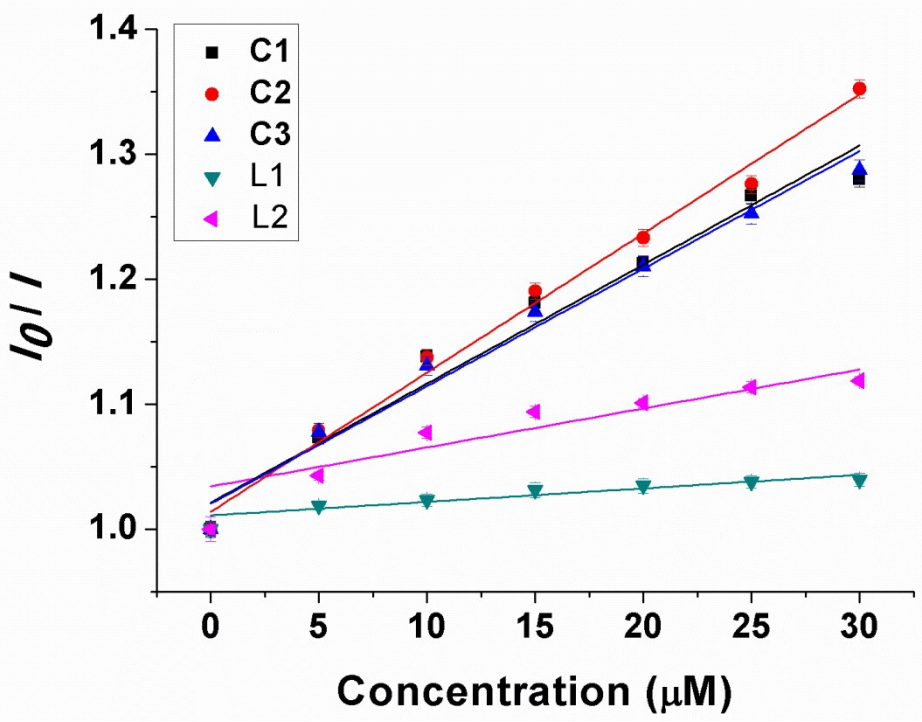


Fig. S21 The fluorescence excitation spectra of complex **C1-C3** (30 μM).

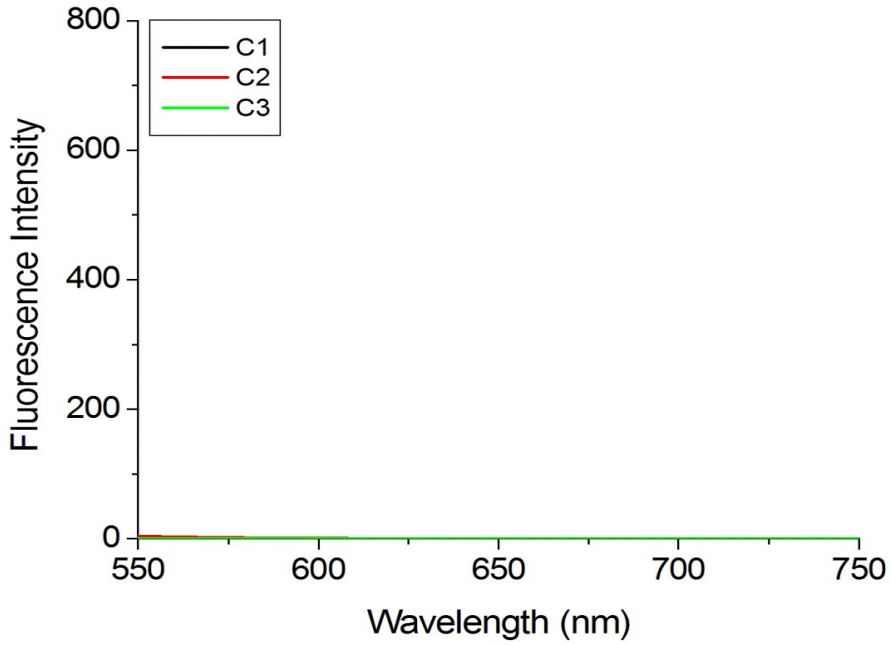


Fig. S22 Overall structure of the HSA.

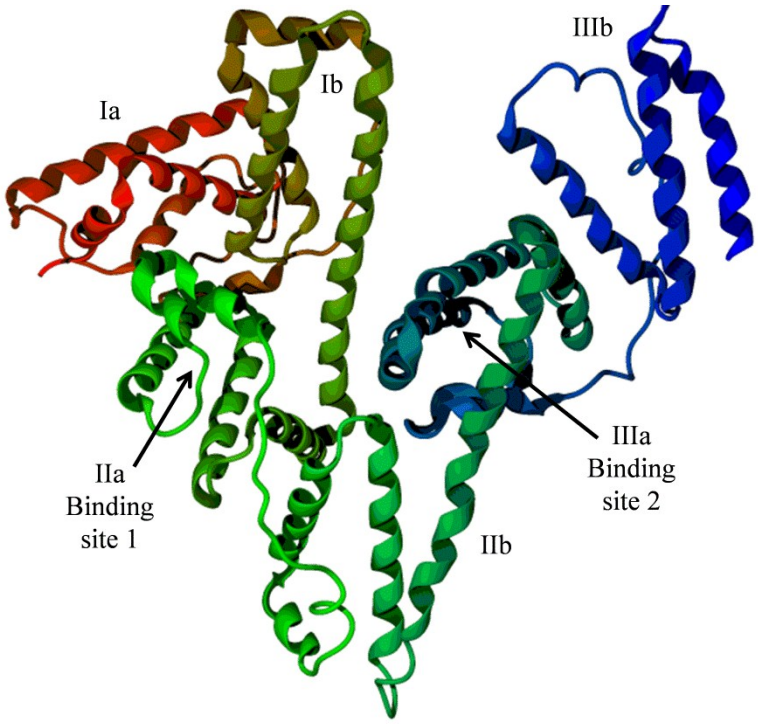


Fig. S23 Molecular docked structure of the complexes interacting with HSA (PDB ID: 1E7H). A) **C1** and B) **C2**.

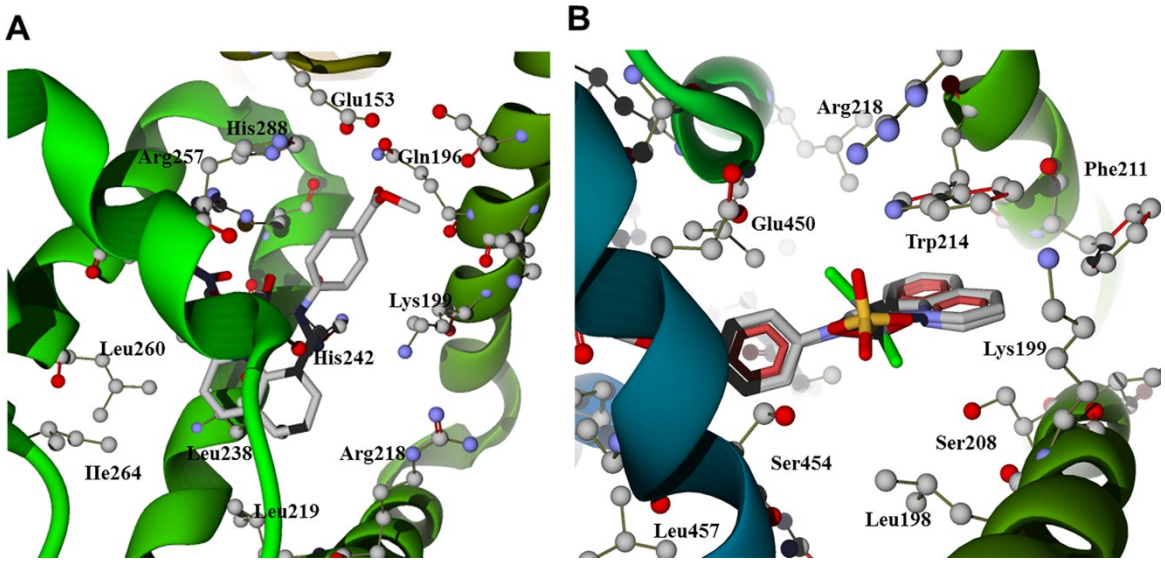


Fig. S24 Molecular docked model of the complex with DNA (PDB ID: 1BNA). A) **C1** and B) **C2**.