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Supporting Information

Structural Diversity in Aroylthiourea Copper Complexes – Formation and Biological Evaluation of $[Cu(I)(\mu\text{-}S)SCl]_2$, *cis*-$Cu(II)S_2O_2$, *trans*-$Cu(II)S_2O_2$ and $Cu(I)S_3$ cores

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Table S1 Selected optimized singlet state (S_0) and triplet state (T_1) geometrical parameters of complex **1** (Bond length, R in Å, Bond angle, θ in degrees and dihedral angle, φ in degrees) along with the X-ray crystal diffraction data (For numbering of atoms see Fig. 6).

Geometrical parameters	XRD	Calculated			
		B3LYP		**M06-2X**	
		S_0	T_1	S_0	T_1
R(Cu1-Cu2)	2.670	2.753	2.980	2.843	2.887
R(Cu1-S1)	2.346	2.359	2.378	2.427	2.441
R(Cu1-Cl1)	2.325	2.380	2.369	2.397	2.406
R(Cu1-S4)	2.294	2.495	2.349	2.532	2.485
R(Cu2-S4)	2.356	2.478	2.363	2.550	2.568
R(Cu2-S2)	2.276	2.380	2.345	2.416	2.397
R(Cu2-Cl2)	2.334	2.394	2.363	2.429	2.392
R(Cu2-S3)	2.346	2.442	2.450	2.517	2.493
R(S1-C1)	1.696	1.707	1.709	1.696	1.695
R(S3-C25)	1.707	1.719	1.728	1.714	1.724
R(S2-C13)	1.701	1.701	1.714	1.694	1.699
R(S4-C37)	1.709	1.725	1.787	1.718	1.738
R(C37-N7)	1.399	1.388	1.405	1.392	1.403
R(C37-N8)	1.399	1.335	1.387	1.317	1.406
R(N8-C45)	1.482	1.481	1.467	1.473	1.462
R(N8-C47)	1.482	1.478	1.464	1.480	1.458
R(N7-H43)	0.899	1.032	1.023	1.031	1.020
R(N7-C38)	1.376	1.389	1.369	1.374	1.359
R(C38-O4)	1.222	1.212	1.222	1.208	1.215
R(C13-N4)	1.325	1.340	1.333	1.327	1.328
R(N4-C23)	1.479	1.478	1.485	1.473	1.474
R(N4-C21)	1.481	1.478	1.479	1.472	1.472
R(C13-N3)	1.399	1.403	1.392	1.402	1.397
R(N3-H15)	0.901	1.028	1.024	1.024	1.024
R(N3-C14)	1.389	1.392	1.396	1.387	1.389
R(C14-O2)	1.211	1.214	1.214	1.208	1.206
R(C25-N6)	1.318	1.339	1.335	1.327	1.324
R(C25-N5)	1.392	1.386	1.385	1.384	1.381
R(N6-C33)	1.491	1.480	1.482	1.474	1.476
R(N6-C35)	1.489	1.477	1.478	1.477	1.477
R(N5-C26)	1.378	1.392	1.396	1.385	1.388
R(C26-O3)	1.225	1.213	1.212	1.206	1.205
R(N5-H29)	0.899	1.032	1.032	1.029	1.028

R(C26-C27)	1.490	1.506	1.506	1.503	1.502
R(C1-N2)	1.313	1.338	1.338	1.325	1.324
R(C1-N1)	1.423	1.397	1.395	1.397	1.398
R(N1-H1)	0.900	1.028	1.029	1.023	1.027
R(N1-C2)	1.369	1.390	1.391	1.387	1.384
R(C2-O1)	1.212	1.217	1.217	1.210	1.211
R(C2-C3)	1.495	1.504	1.503	1.497	1.498
R(N2-C11)	1.468	1.476	1.476	1.468	1.468
R(N2-C9)	1.486	1.479	1.479	1.475	1.476
θ(C25-S3-Cu1)	112.5	110.1	111.7	104.2	105.9
θ(S3-Cu2-Cl2)	110.9	111.2	110.9	112.2	115.2
θ(Cl2-Cu2-S2)	119.0	108.2	113.5	103.6	109.3
θ(S2-Cu2-S4)	116.8	113.9	104.4	114.6	103.2
θ(Cu2-S4-C37)	116.5	109.7	110.9	104.9	98.7
θ(C37-S4-Cu1)	108.9	109.7	108.4	106.0	106.5
θ(S4-Cu1-Cl1)	111.5	108.3	114.2	107.7	99.5
θ(Cl1-Cu1-S1)	119.1	116.1	114.3	116.5	112.8
θ(Cu1-S1-C1)	107.5	110.7	112.1	104.3	102.7
θ(S1-Cu1-S3)	116.8	115.7	111.4	103.9	101.3
θ(C25-S3-Cu2)	112.6	111.4	111.4	106.9	106.3
θ(Cu2-S2-C13)	109.8	110.7	106.6	105.1	107.2
θ(S2-C13-N3)	118.6	119.7	119.2	119.6	120.1
θ(S2-C13-N4)	122.8	122.2	121.7	123.0	122.1
θ(S4-C37-N7)	119.3	118.7	119.4	118.0	120.4
θ(S4-C37-N8)	122.9	122.6	114.4	122.5	108.9
θ(S1-C1-N1)	118.4	119.4	119.6	118.9	119.0
θ(S1-C1-N2)	124.6	122.5	122.3	124.7	125.1
θ(S3-C25-N6)	123.2	121.8	121.8	122.1	122.2
θ(S3-C25-N5)	119.1	119.5	119.2	118.8	118.7
φ(C25-S3-Cu2-Cl2)	1.3	7.0	1.7	17.4	0.2
φ(C25-S3-Cu1-S1)	-9.9	-5.9	-6.5	-16.8	-20.3
φ(Cl1-Cu1-S4-C37)	1.8	-13.7	-6.0	-15.9	-31.8
φ(Cl1-Cu1-S1-C1)	2.3	17.6	9.6	37.0	43.8

Table S2 Frontier molecular orbital compositions (%) for the complex 1 in ground state

Orbital	Energy (eV)	Contribution (%)				Main bond type
		2Cu	4S	2Cl	Ligand	
L+5	-1.059	1.33	4.89	0.23	93.55	π*(ligand)
L+4	-1.119	4.60	6.00	0.32	89.08	π*(ligand)
L+3	-1.631	5.60	9.31	0.27	84.82	π*(ligand)
L+2	-1.746	4.16	9.52	0.62	85.70	π*(ligand)
L+1	-1.835	4.77	8.57	0.57	86.09	π*(ligand)
L	-1.963	1.63	6.96	0.15	91.26	π*(ligand)
H	-5.417	35.50	39.72	5.11	19.67	d(Cu) + p(S) + π(ligand)
H-1	-5.512	39.71	40.67	5.94	13.68	d(Cu) + p(S) + π(ligand)
H-2	-5.612	47.57	27.22	14.99	10.22	d(Cu) + p(S) + p(Cl) + π(ligand)
H-3	-5.825	40.71	27.45	17.03	14.81	d(Cu) + p(S) + p(Cl) + π(ligand)
H-4	-5.951	37.81	28.76	18.66	14.78	d(Cu) + p(S) + p(Cl) + π(ligand)
H-5	-6.180	41.48	26.70	12.85	18.97	d(Cu) + p(S) + p(Cl) + π(ligand)

Table S3 Atomic charges of selected atoms of the important bonds of the complex **1** (For numbering of atoms see **Fig.** 6).

Atoms	Atomic Charges	
	S_0	T_1
Cu1	0.756	0.823
Cu2	0.754	0.918
Cl1	-0.796	-0.808
Cl2	-0.801	-0.784
S1	-0.321	-0.330
S2	-0.307	-0.275
S3	-0.356	-0.364
S4	-0.372	-0.355
C13	0.359	0.375
C37	0.388	0.195
C1	0.363	0.365
C25	0.380	0.396
N1	-0.686	-0.688
N2	-0.419	-0.418
N3	-0.687	-0.681
N4	-0.413	-0.403
N5	-0.683	-0.682
N6	-0.413	-0.403
N7	-0.687	-0.690
N8	-0.404	-0.443

Table S4 DNA binding constant (K_b), quenching constant (K_q) and apparent binding constant (K_{app}) values.

Complex	K_b (M^{-1})	K_q (M^{-1})	K_{app} (M^{-1})
1	3.59×10^4	4.50×10^4	2.25×10^6
2	3.16×10^4	4.14×10^4	2.07×10^6
3	2.36×10^4	3.81×10^4	1.91×10^6
4	1.96×10^4	3.32×10^4	1.66×10^6

Table S5 Protein binding constant (K_b), quenching constant (K_q) and number of binding sites (n) values.

Complex	K_b (M^{-1})	K_q (M^{-1})	N
1	1.09×10^6	2.21×10^5	1.18
2	5.78×10^5	1.41×10^5	1.11
3	3.36×10^5	1.09×10^4	1.09
4	1.23×10^5	9.24×10^4	1.03

Table S6 *In vitro* cytotoxicity of the Cu complexes in MCF7 and A549 cancer cell lines

Compound	IC50 (μM)	
	A549	MCF7
1	63.73	70.71
2	103.85	81.69
3	160.85	155.44
4	50.00	20.45
Cyclophosphamide	41.84	11.89

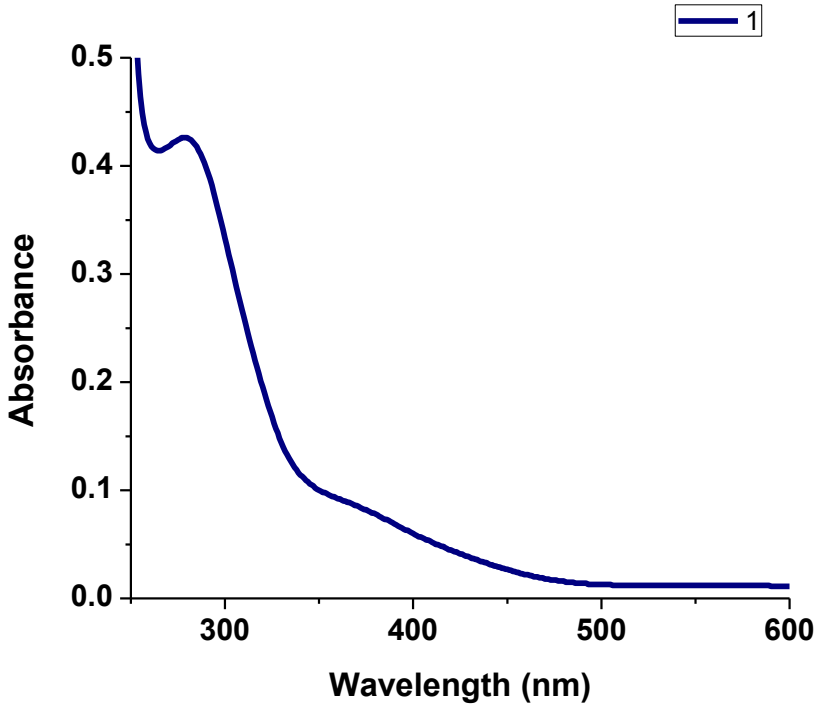

Fig. S1 Absorption spectrum of **1** in DMF ($\pi \rightarrow \pi^*$ = 227 nm, $n \rightarrow \pi^*$ = 280 nm and MLCT = 370 nm).

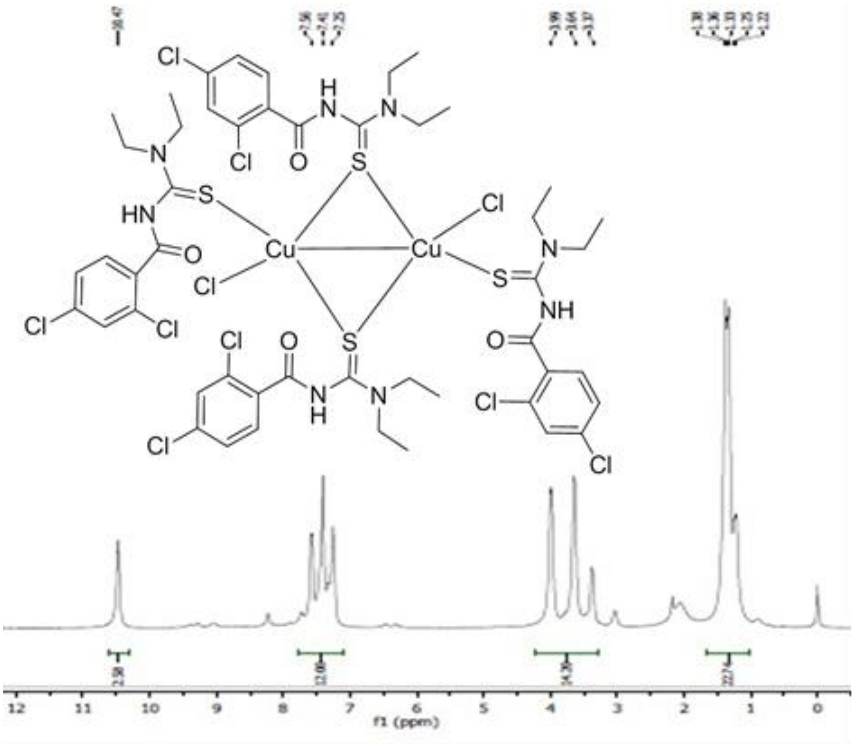

Fig. S2 ^{1}H NMR spectrum of **1**.

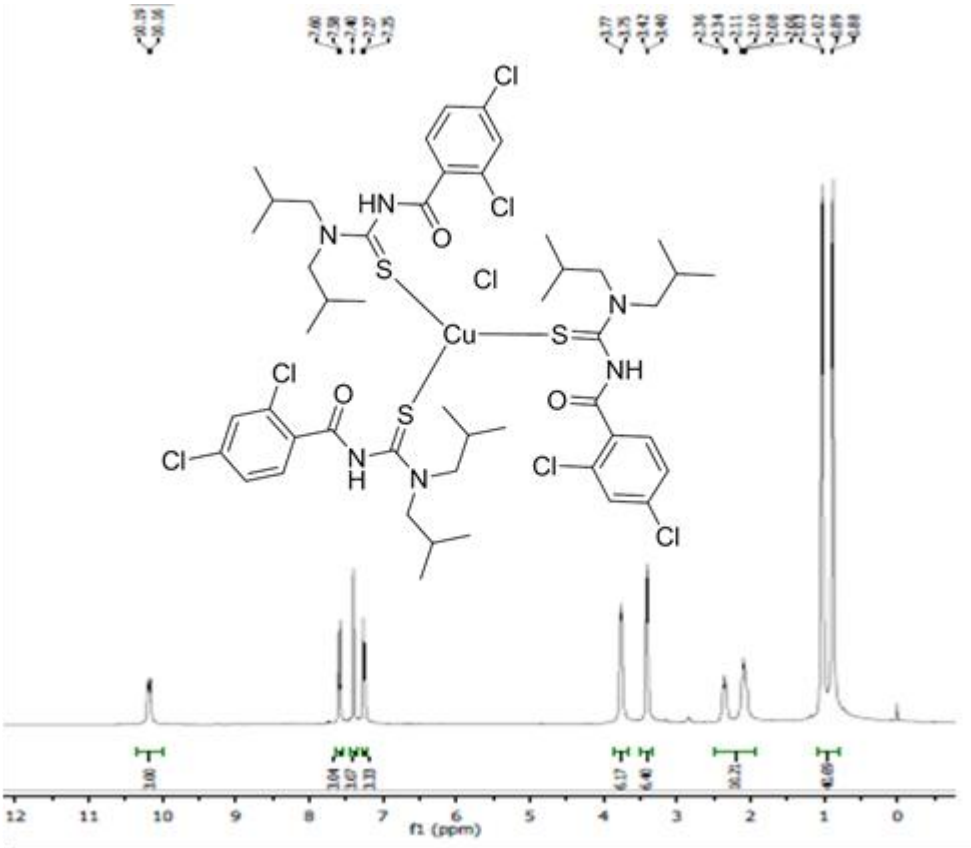

Fig. S3 ^{1}H NMR spectrum of **3**.

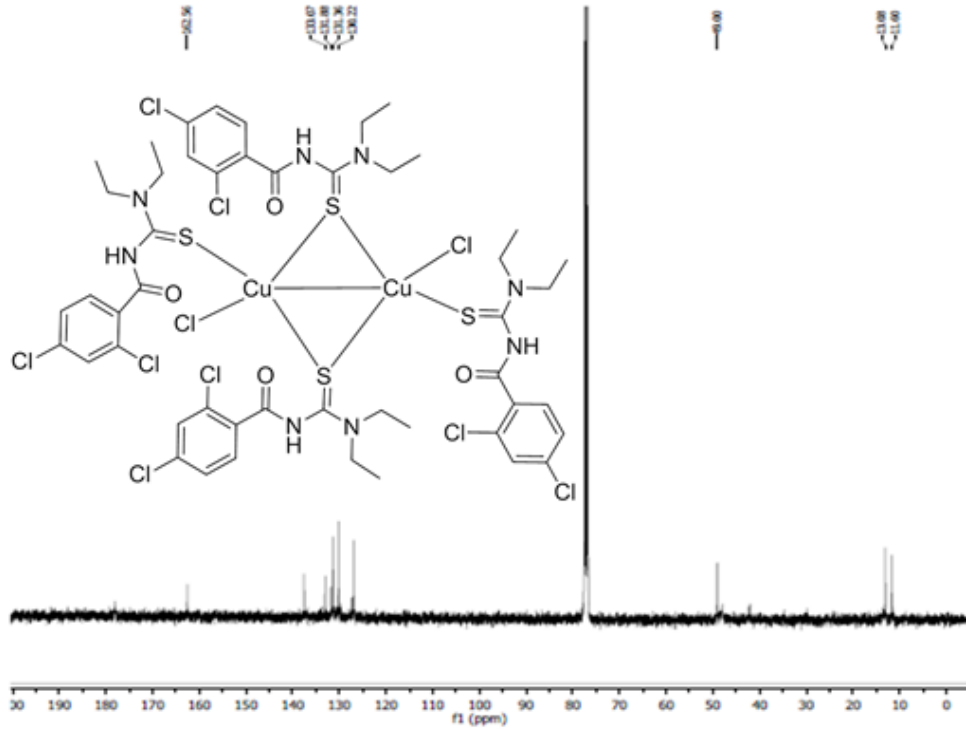

Fig. S4 ^{13}C NMR spectrum of **1**.

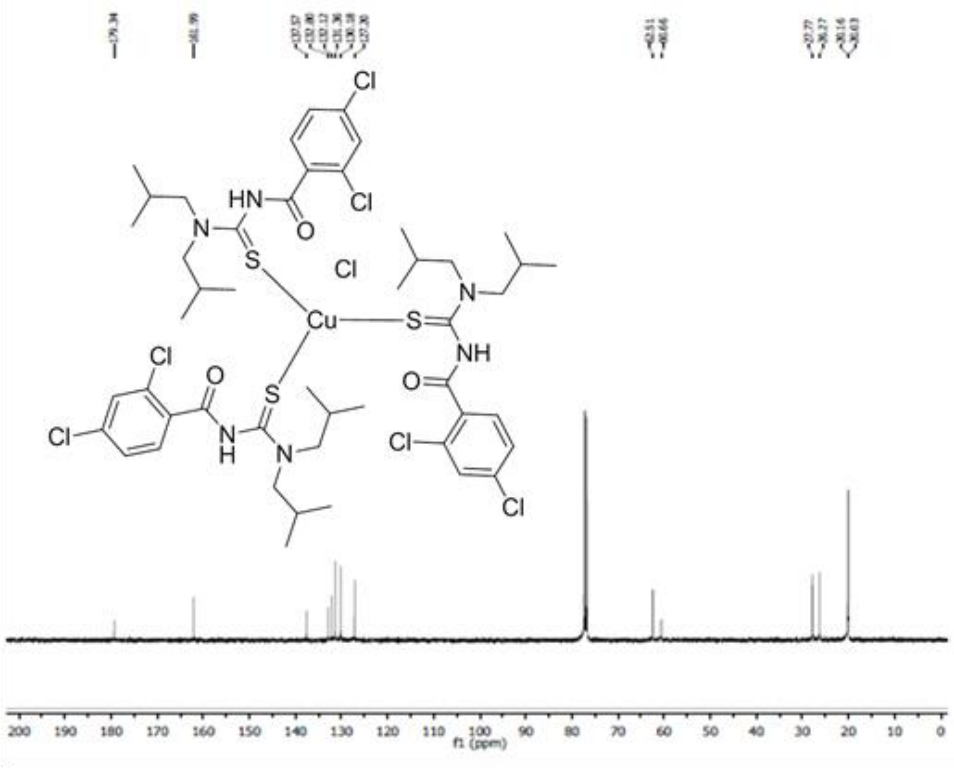

Fig. S5 ^{13}C NMR spectrum of **3**.

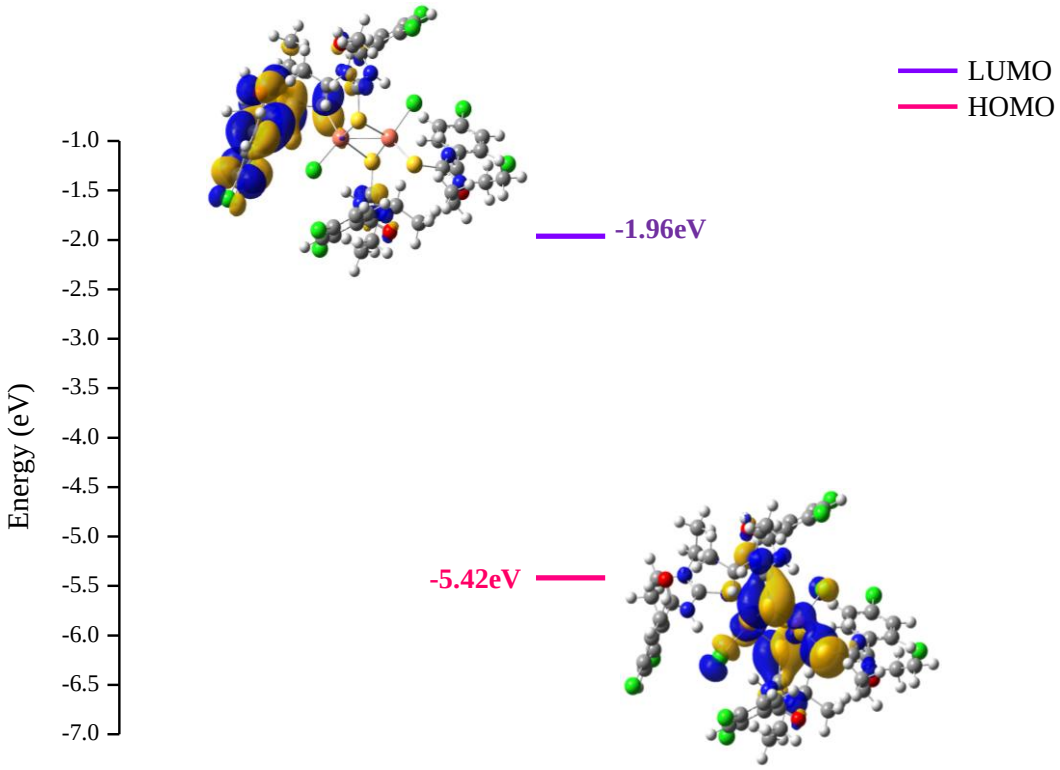

Fig. S6 Energy level plot of HOMO and LUMO for complex **1**.

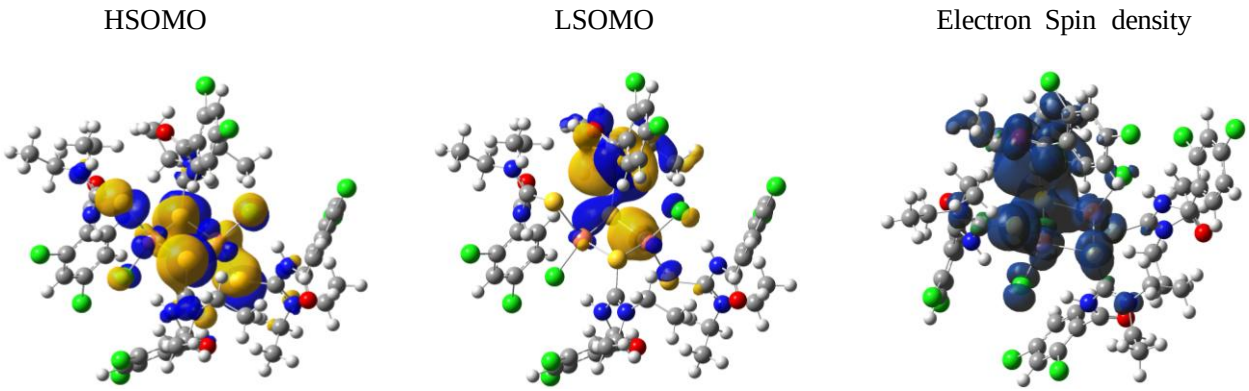

Fig. S7 Isodensity surface plots of the HSOMO and LSOMO and electron spin density of **1** in T_1 state. Blue and green colors show regions of positive and negative spin density values respectively.

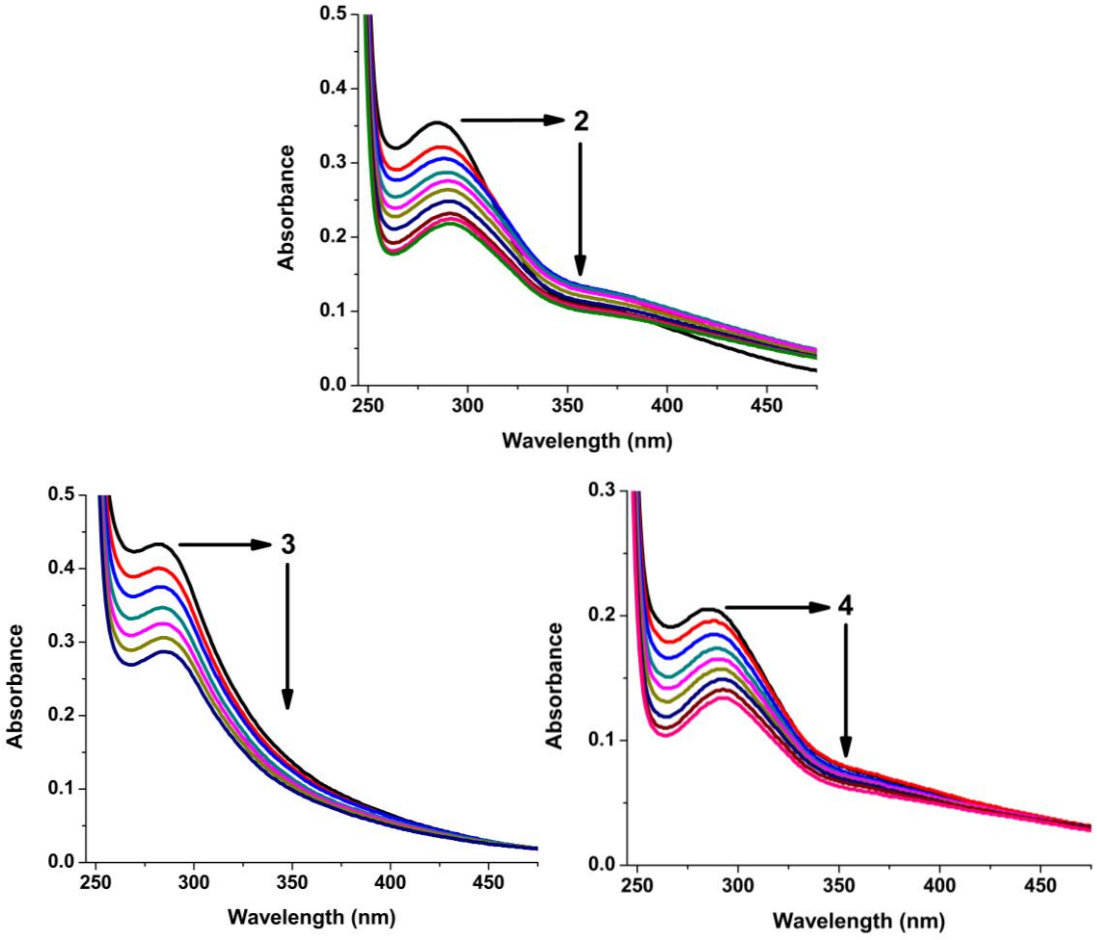

Fig. S8 Absorbance titrations of the complexes (**2-4**) (5 µM) with CT DNA (0-50 µM).

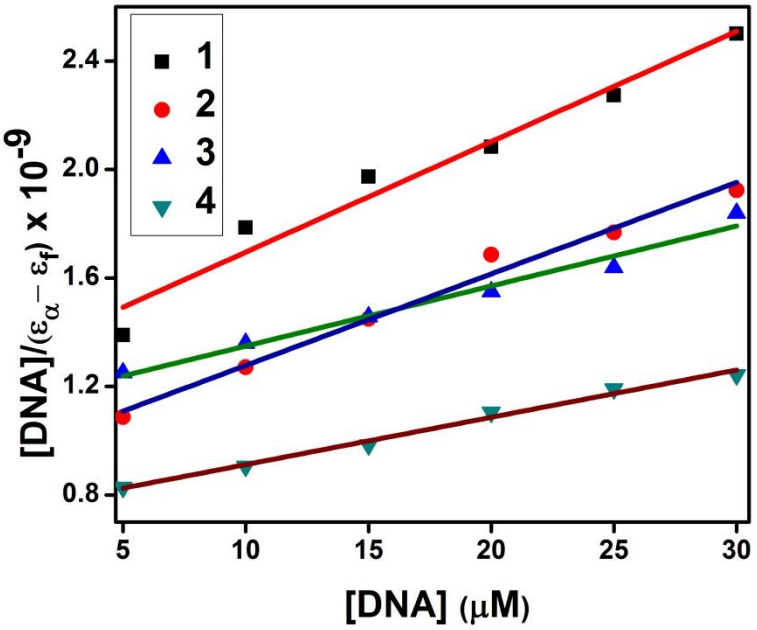

Fig. S9 Stern-Volmer plots of absorbance titrations of the complexes (**1-4**) with CT DNA.

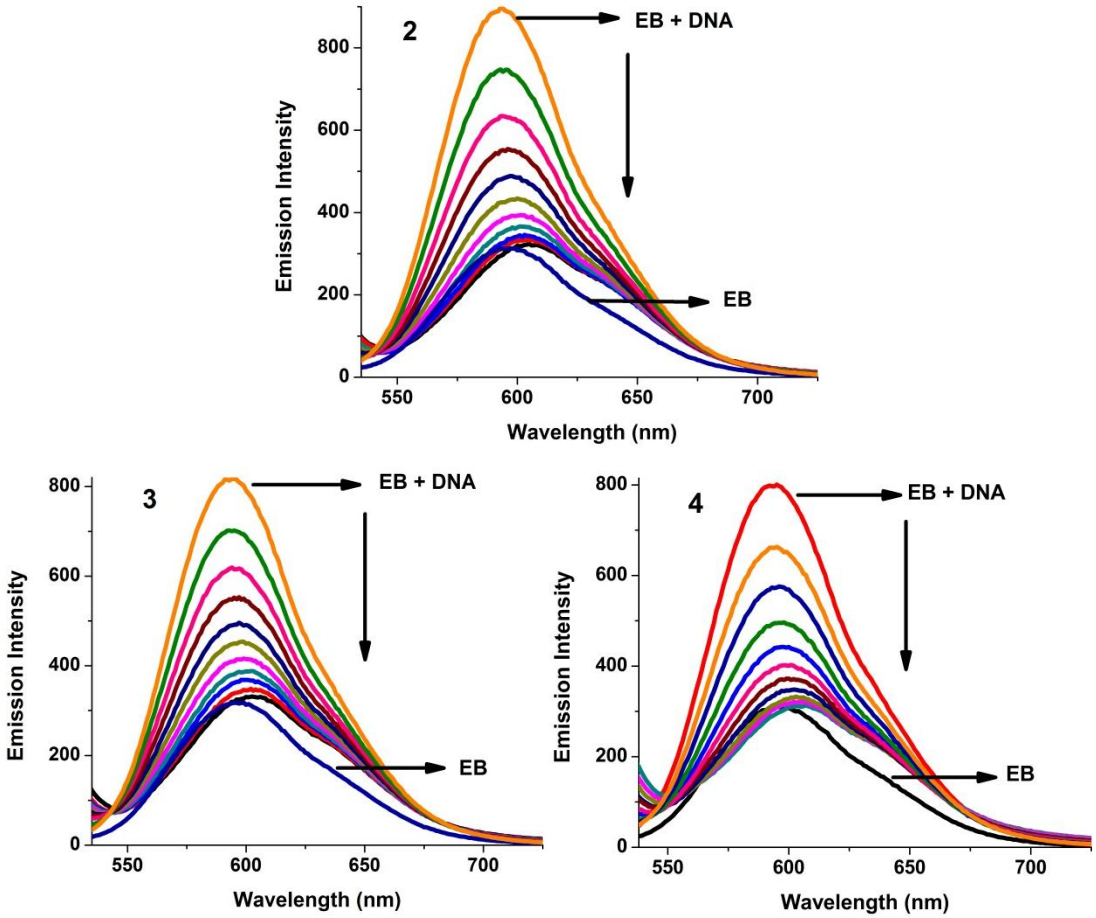

Fig. S10 Fluorescence titrations of the complexes (**1-4**) (0-50 μM) with EB bounded CT DNA.

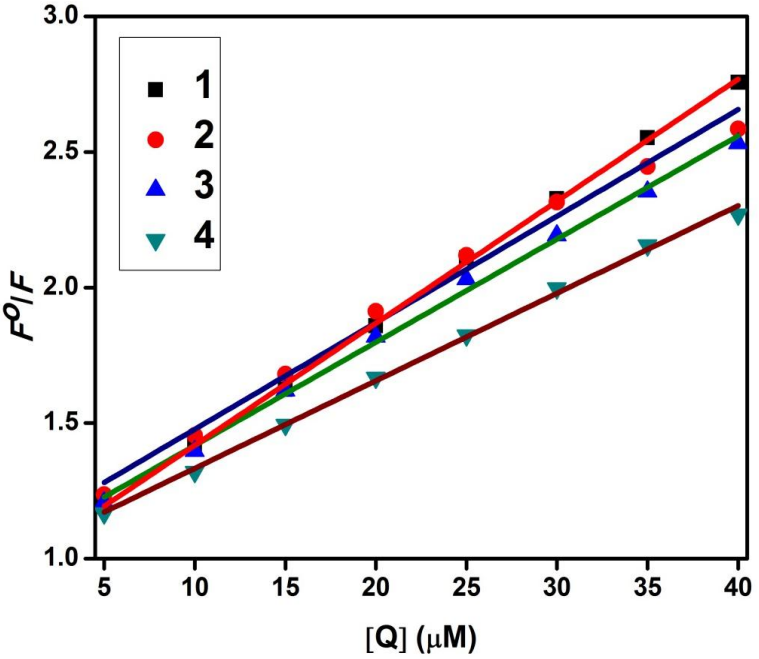

Fig. S11 Stern-Volmer plots of fluorescence titrations of the complexes (**1**-**4**) with CT DNA.

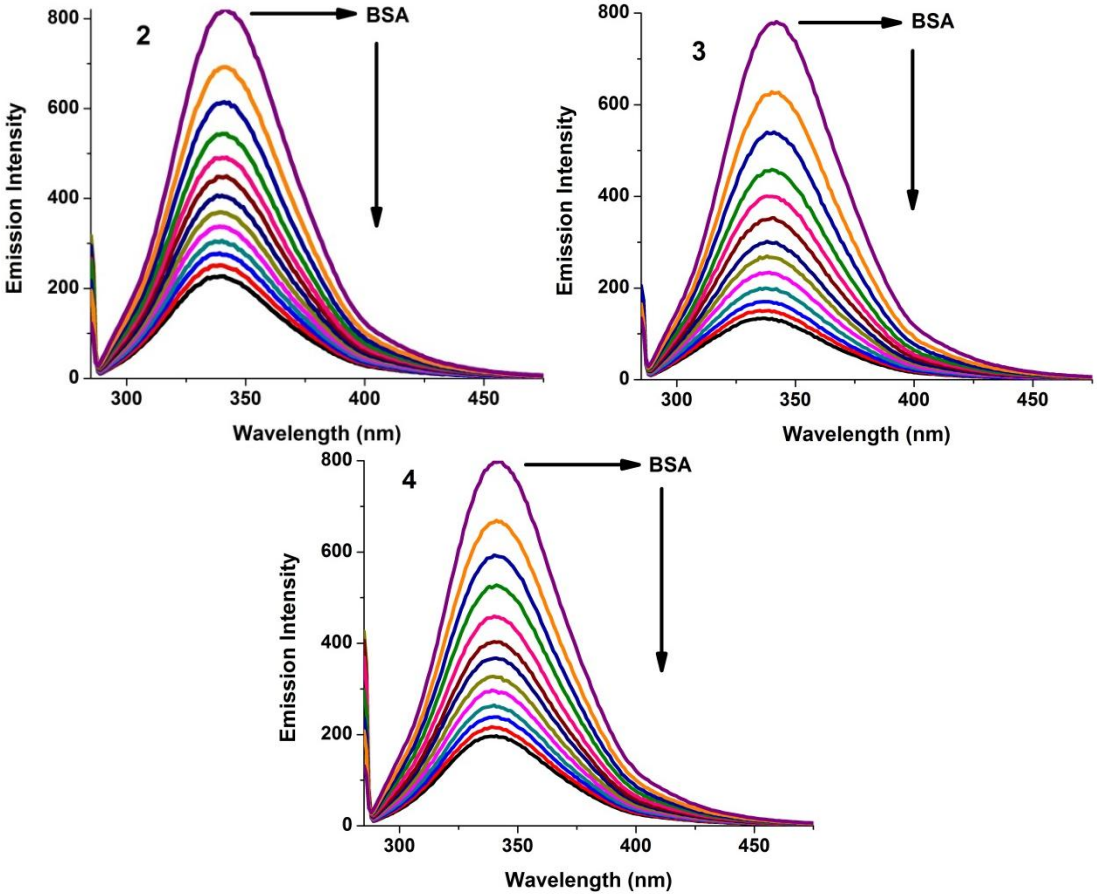

Fig. S12 Fluorescence titrations of the complexes (**1**–**4**) (2 μM) with BSA (1 μM).

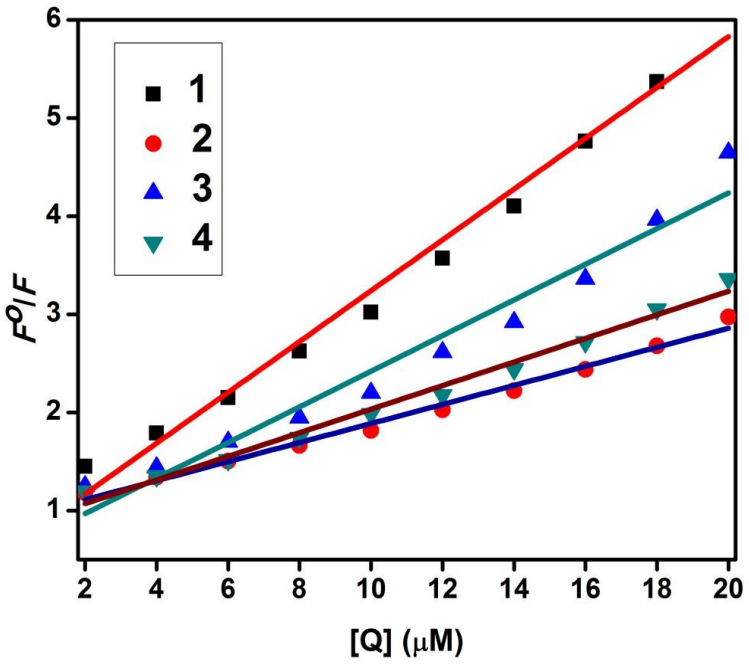

Fig. S13 Stern-Volmer plots of the fluorescence titrations of the complexes (**1**-**4**) with BSA.

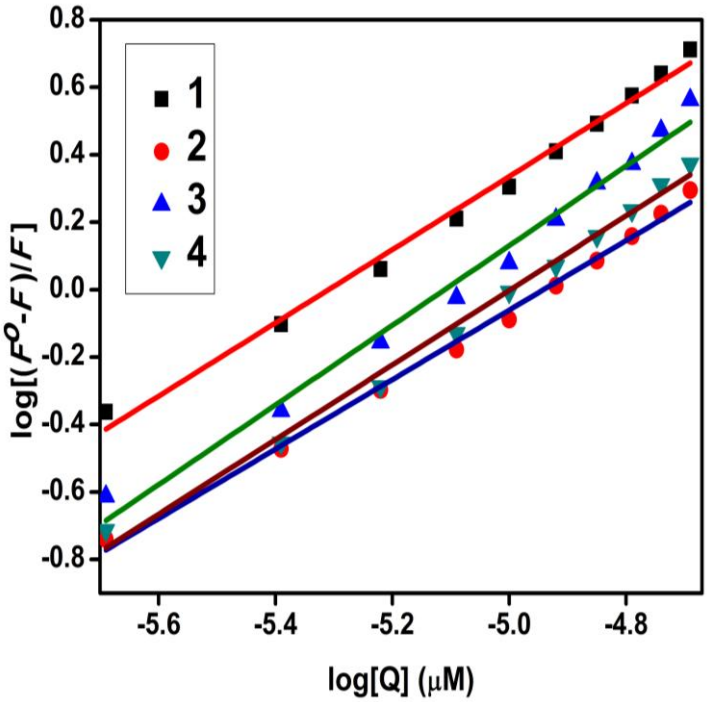

Fig. S14 Plots of the fluorescence titrations of the complexes (**1**–**4**) with BSA.

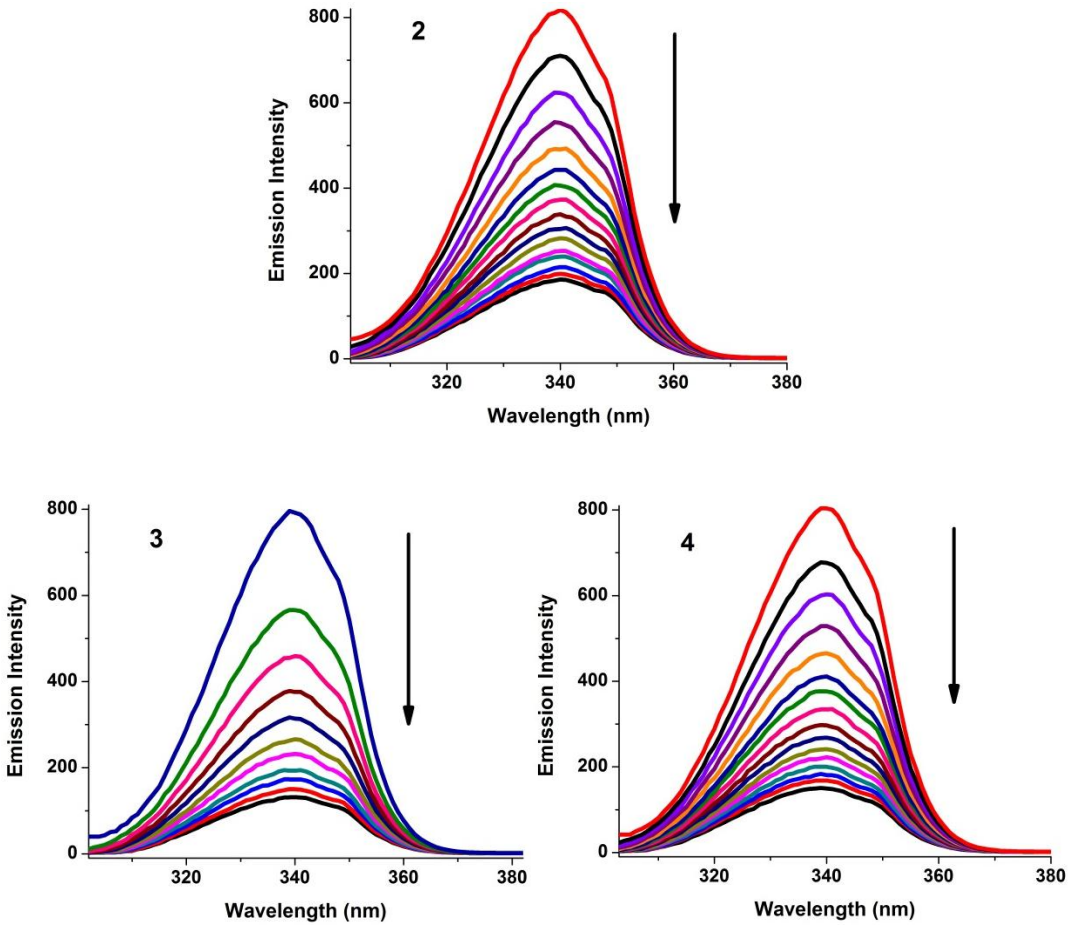

Fig. S15 Synchronous spectra of BSA (1 μM) as a function of concentration of the complexes (**1**–**4**) (0-20 μM) with $\Delta\lambda$ = 60 nm.

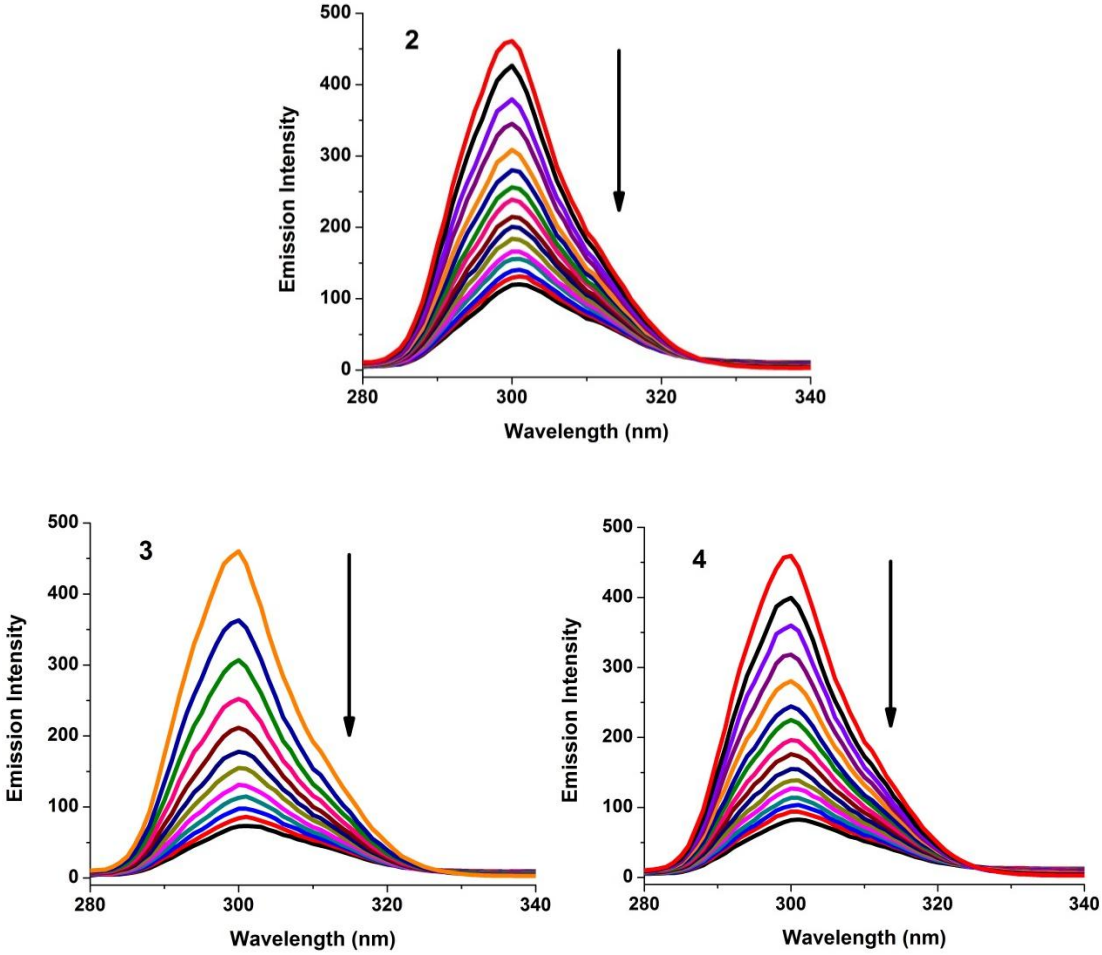

Fig. S16 Synchronous spectra of BSA (1 μM) as a function of concentration of the complexes (**1**–**4**) (0-20 μM) with $\Delta\lambda$ = 15 nm.

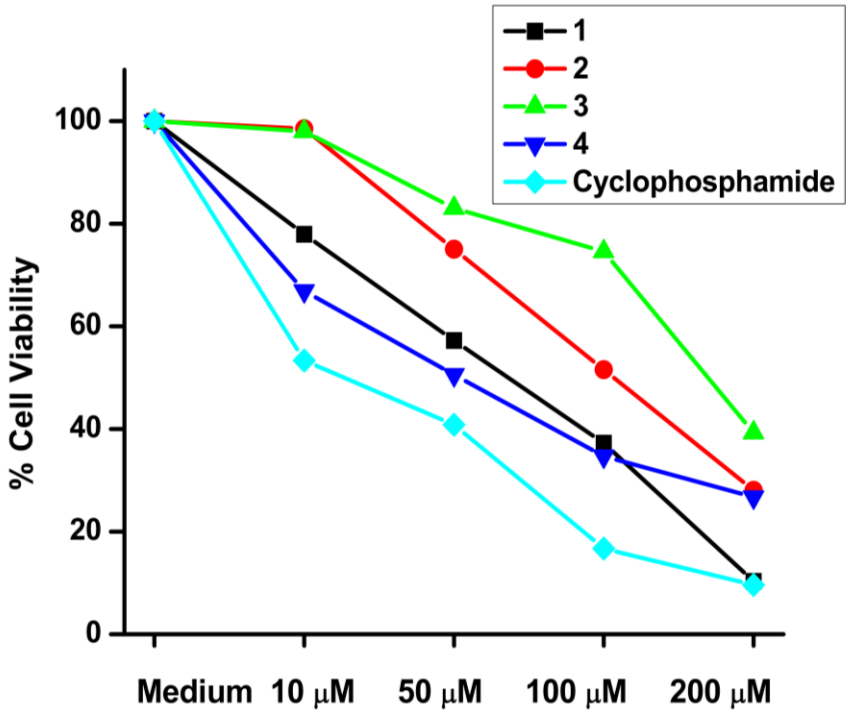

Fig. S17 Cytotoxicity of the complexes (**1**–**4**) after 24 h incubation on A549 cell lines.

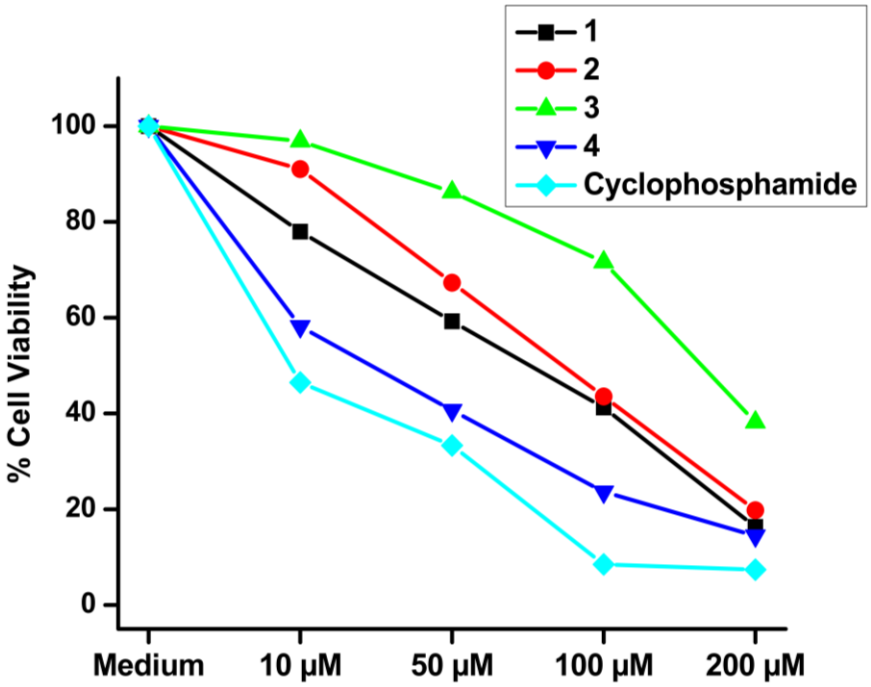

Fig. S18 Cytotoxicity of the complexes (**1**–**4**) after 24 h incubation on MCF7 cell lines.