Electronic Supplementary Material (ESI) for Dalton Transactions.

Exploring the BSA-, DNA-binding, cytotoxicity and cell cycle evaluation of ternary copper(II)/diimine complexes with N,N-dibenzyl-N'-benzoylthiourea as promising metallodrug candidates

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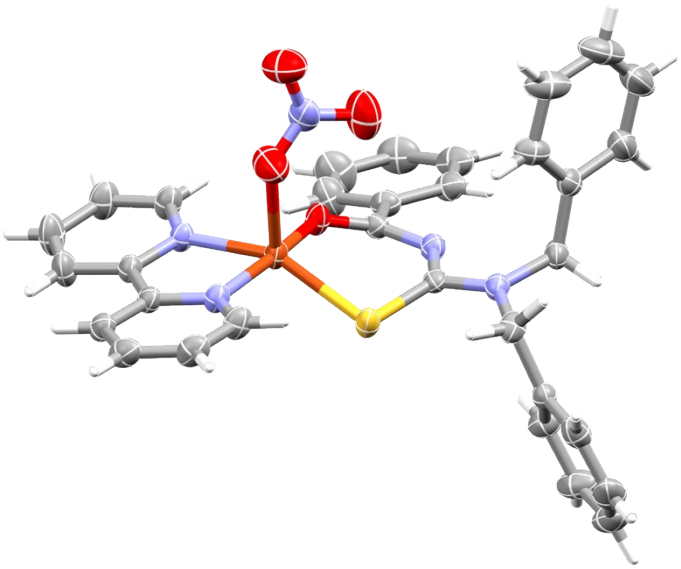

Figure S1. Crystal structure of complex 2.

Crystal packing of 1

Figure S2. Crystal packing and representation of weak intermolecular contacts of the complexes 1 and 2.

Crystal packing of 2

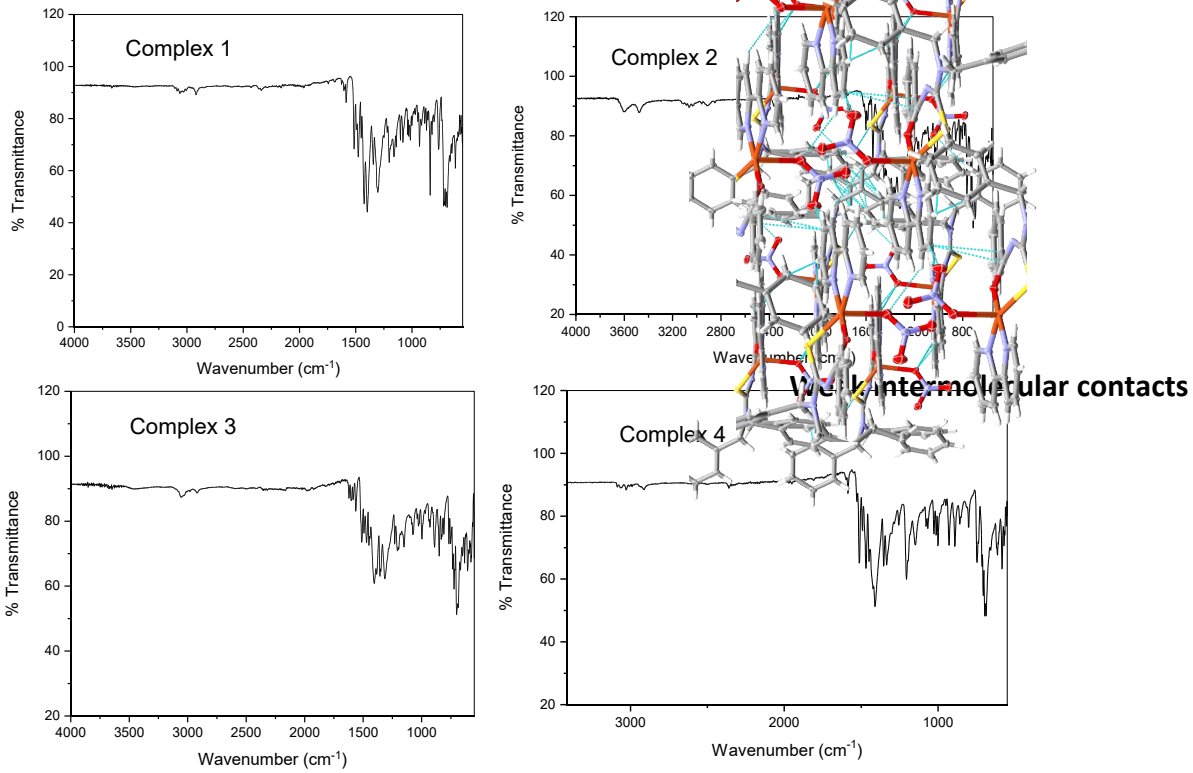

Figure S3. Infrared spectra of complexes 1-4.

Table S1. Infrared assignment for complexes and Th free ligand.

Assignments	Th	(1)	(2)	(3)	(4)
νN-H	3077	-	-	-	-
νC-H $_{aromatic}$	3056 w	2966 w	3055 w	2966 w	3028 w
νC-H $_{(CH3)}$	-	-	-	-	2912 w
νNO_3^-	-	1601 w	1600 w	1601 w	1602 w
νNO_3^-	-	1587 w	1585 w	1590 w	1579 w
νC=O $_{(amide)}$	1687 s	1514 m	1512 m	1542 m	1512 m
νC=C $_{(ring)}$	1488 s	1477 m	1492 m	1494 m	1490 m
νC=C $_{(ring)}$	1426 s	1450 m	1469 m	1452 m	1467 m
νC=C $_{(ring)}$	1417 s	1433 m	1446 m	1436 m	1448 m
νC=N	-	1425 s	1404 s	1409 s	1409 s
γCH_3	-	-	-	-	1255 m
νC-N $_{aromatic}$	-	1260 m	1195 m	1218 m	1205 m
νC-N $_{(thioreua)}$	1265 m	1201 m	1151 m	1153 m	1147 m
νC=S	1189 s	1014 w	1074 w	1029 m	1000 m
γ Aromatic Ring	946 w	946 w	997 m	935 w	927 m
γ Aromatic Ring	931 w	933 w	926 m	894 w	889 m
γ Aromatic Ring	873 s	838 s	848 m	858 m	858 m
γCH(ϕ)	792 w	821 w	827 m	825 w	746 m
γCH(ϕ)	771 w	804 w	734 s	765 s	713 s
γCH(ϕ)	692 s	763 m	723 s	730 s	705 s

s = strong; m = medium, w = week; ν = designates a stretching vibration; γ = designates a deformation vibration.

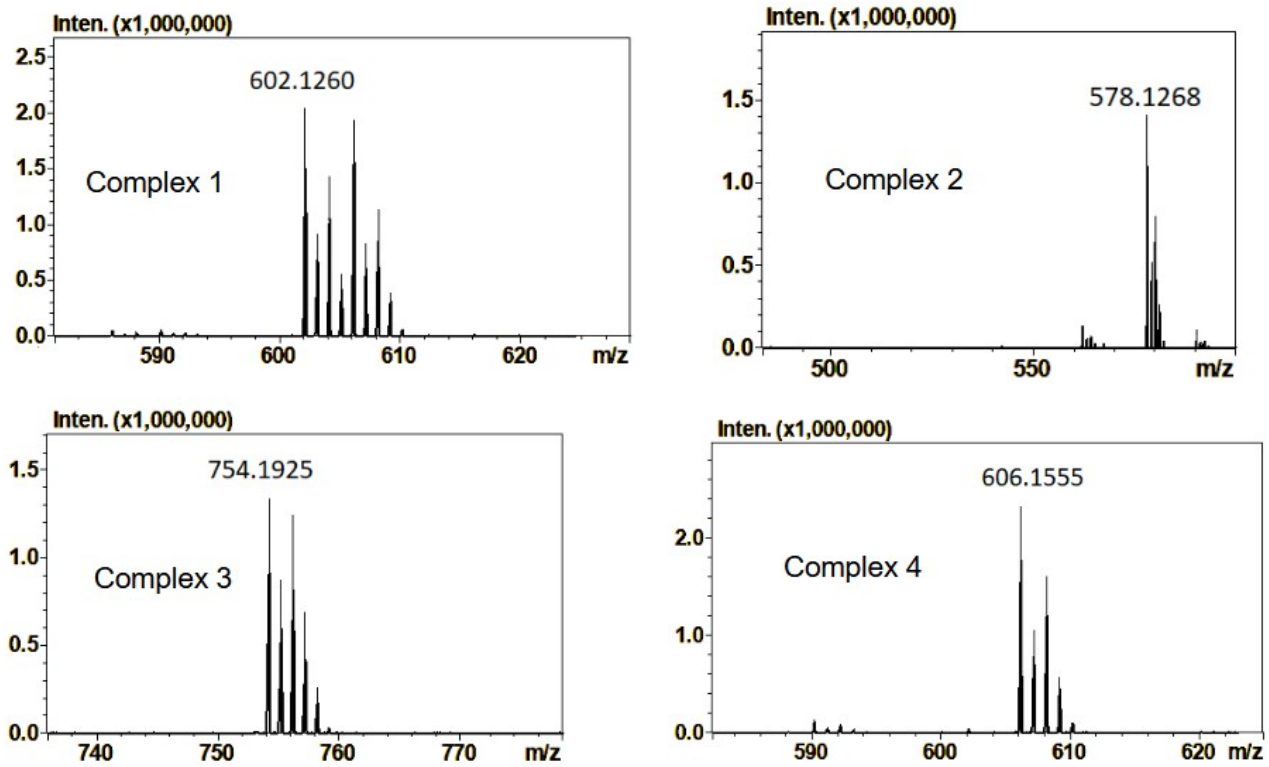

Figure S4 – Mass spectrum of complexes 1, 2, 3 and 4, presenting the monoisotopic mass of the specie $[M\text{-}NO_3]^+$.

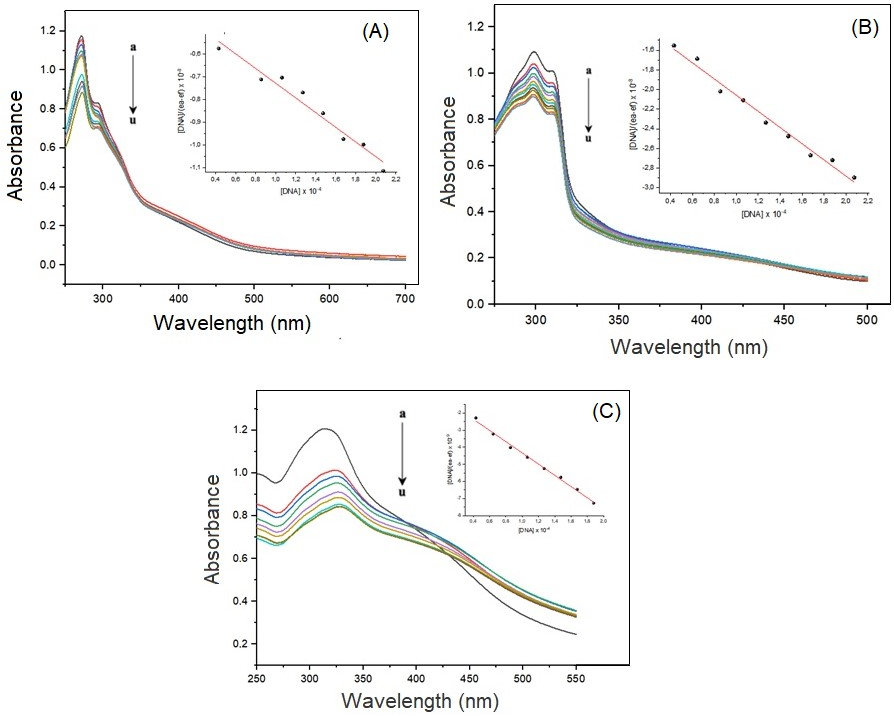

Figure S5 – UV-vis absorption spectrum of complexes 1 (A), 2 (B) and 4 (C) (21 µM) in the presence of increasing additions of CT-DNA solution and linear regression for K_b determination

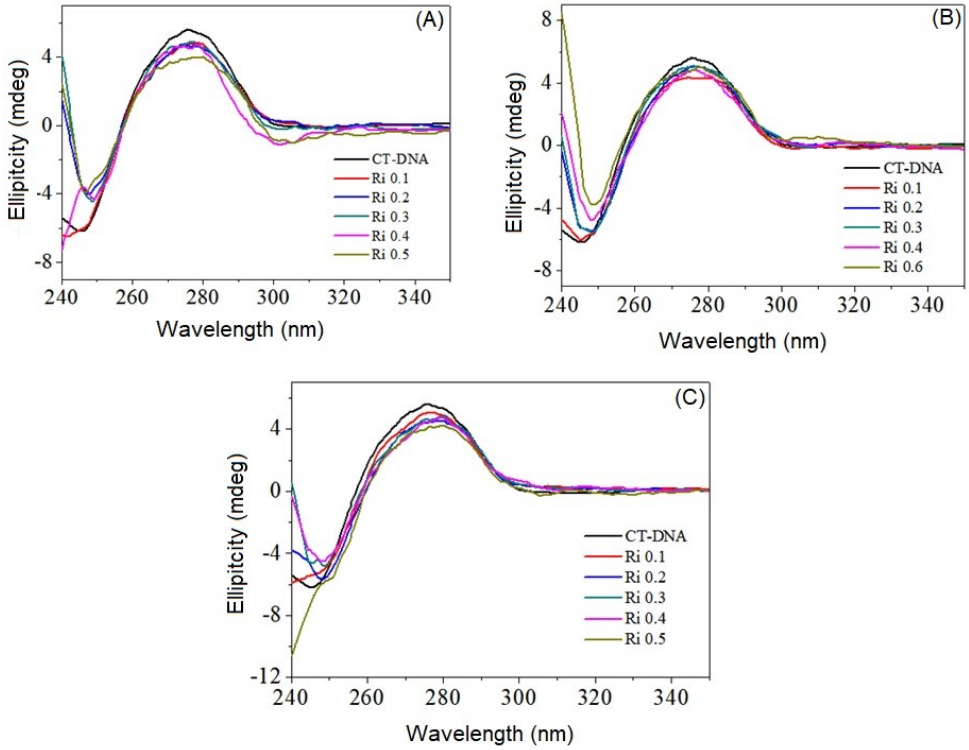

Figure S6 - CD spectra of CT-DNA (50 µM) in the presence of compounds 1 (A), 2 (B) and 4 (C) (2.5 - 20 µM) in Tris-HCl buffer (pH 7.4) at different molar ratios (Ri), where Ri = [Complex]/[CT-DNA].

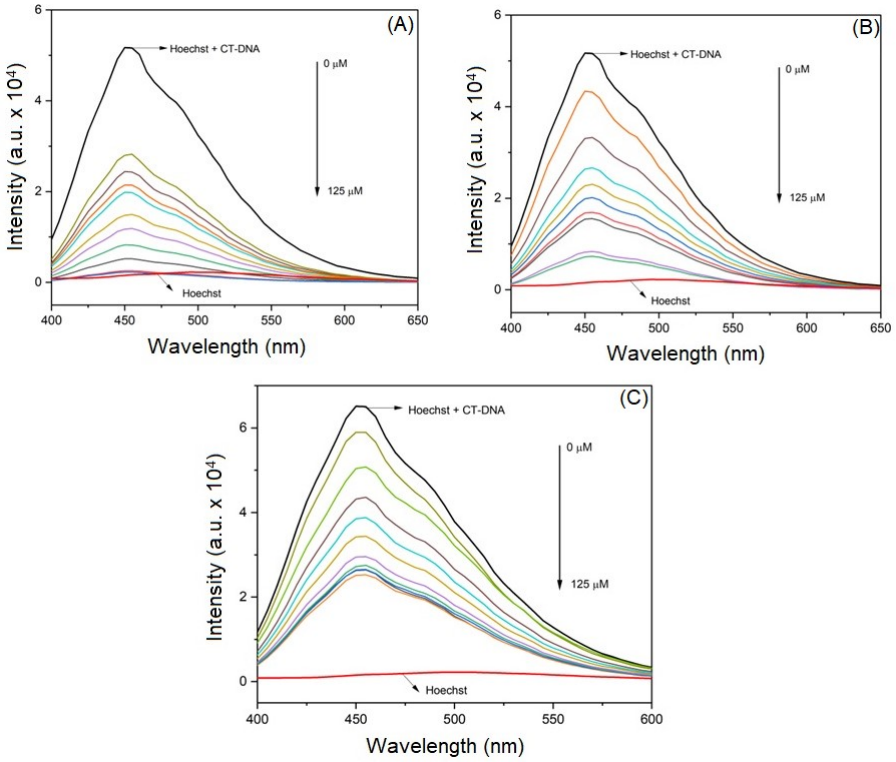

Figure S7 – Emission spectrum of Hoechst 33258 (2.7 μM) in the absence and presence of CT-DNA solution (125 μM) (λ_{ex}= 340 nm) at 37°C with increasing concentration of compounds 1 (A), 2 (B) and 4 (C).

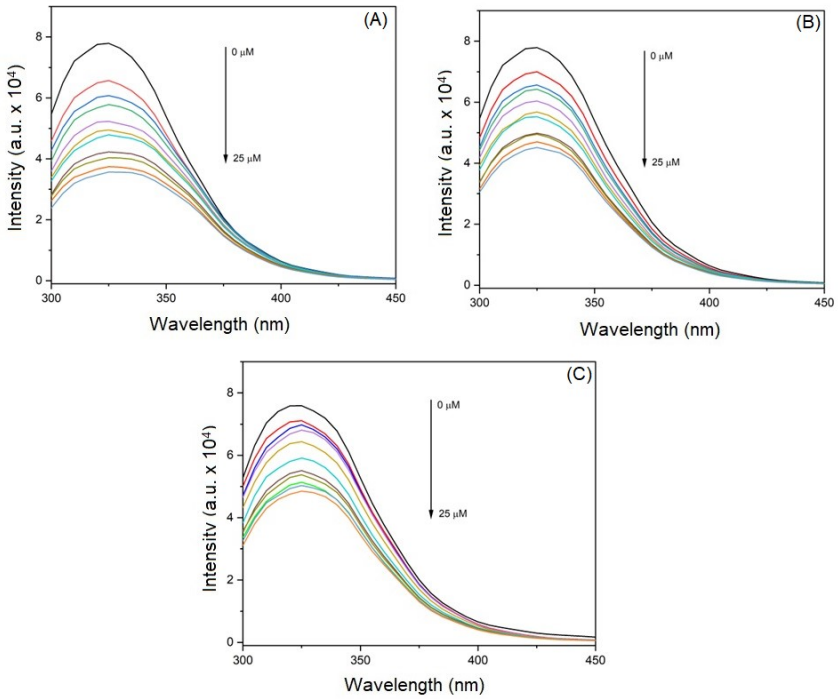

Figure S8 – Emission spectrum of BSA (2.5 μM) in the absence and in the presence of increasing concentrations of compound compounds 1 (A), 2 (B) and 4 (C) (λ_{em}= 280 nm; λ_{ex}= 340 nm) at 298 K.

Table S2 - X-Ray crystallographic data collection and refinement parameters for complexes 1 and 2.

	Complex 1	Complex 2
Empirical formula	$C_{34}H_{27}CuN_5O_4S$	$C_{32}H_{27}CuN_5O_4S$
Molecular Weight	665.20	641.18
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal System	Monoclinic	Monoclinic
Space group	P $2_1/c$	P $2_1/c$
Unit cells dimensions	a = 15.4463(5) Å;	a = 9.2596(4) Å
	b = 9.6553(2) Å;	b = 29.1579(11) Å
	c = 21.3098(6) Å;	c = 10.9693(5) Å
Volume	3040.77(15) $Å^3$	2929.1(2) $Å^3$
Z	4	4
Density (calculated)	1.453 Mg/m^3	1.454 Mg/m^3
Absorption coefficient	0.835 mm^{-1}	0.864 mm^{-1}
F(000)	1372	1324
Crystal size	0.580 x 0.510 x 0.280 mm^3	0.642 x 0.142 x 0.104 mm^3
Theta range for data collection	2.737 to 27.102°.	2.780 to 27.102°.
Index ranges	-19≤h≤19, -12≤k≤12, -27≤l≤27	-11≤h≤11, -37≤k≤37, -14≤l≤14
Reflections collected	65891	63608
Independent reflections	6695 [R(int) = 0.0292]	6446 [R(int) = 0.0348]
Completeness to theta = 25.242°	99.8 %	99.9 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / Restraints / Parameters	6695 / 0 / 446	6446 / 0 / 388
Goodness-on-fit on F^2	1.130	1.094
Final R indices [I> 2σ (I)]	R1 = 0.0387, wR2 = 0.0880	R1 = 0.0478, wR2 = 0.1228
R indices (all data)	R1 = 0.0594, wR2 = 0.1080	R1 = 0.0641, wR2 = 0.1378
Largest diff. peak and hole	0.510 and -0.313 $e.Å^{-3}$	0.971 and -0.526 $e.Å^{-3}$

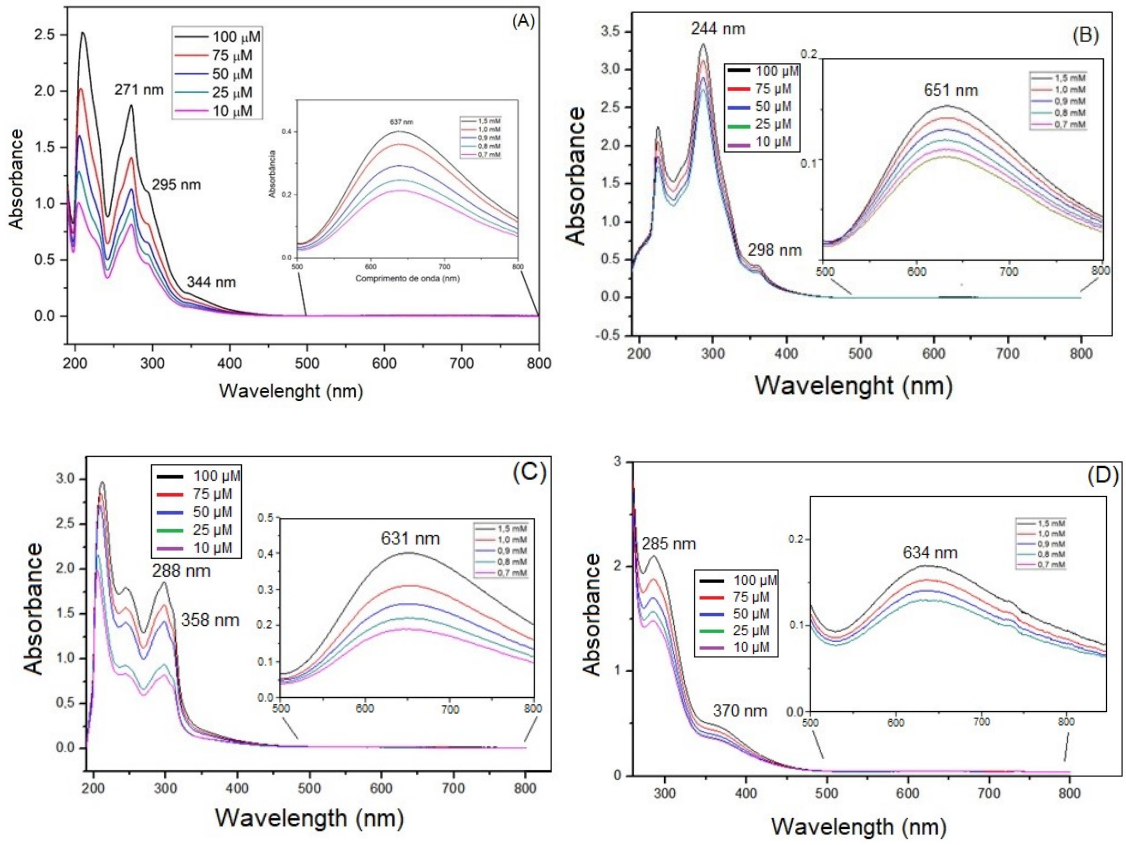

Figure S9. Electronic absorption spectra in the UV-Vis region for complexes (A) 1, (B) 2, (C) 3 and (D) 4, in methanol.

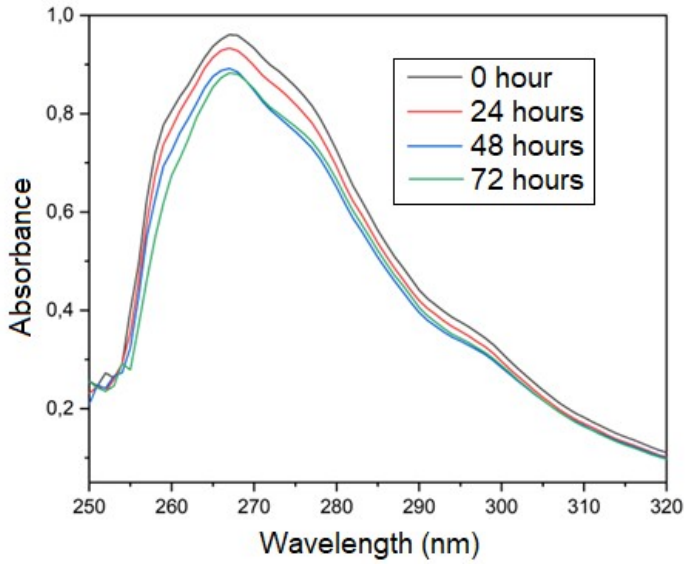

Figure S10- UV-Vis spectra of complex 1 in DMSO at different times.

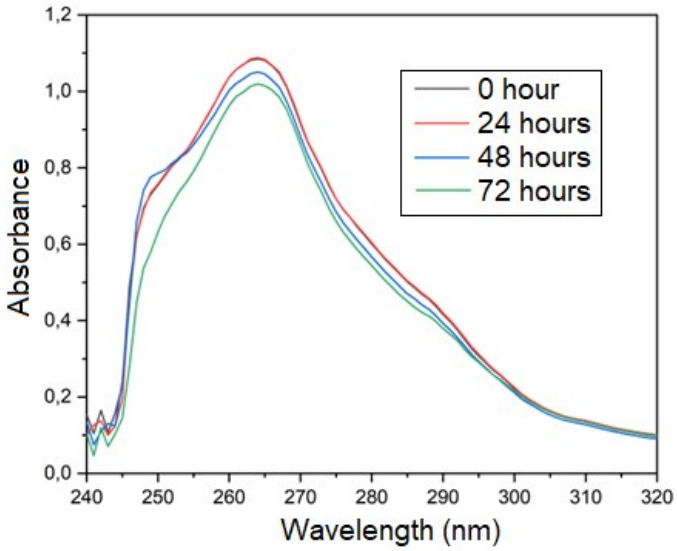

Figure S11 - UV-Vis spectra of complex 1, in DMSO/RPMI (50:50, *v*/*v*) at different times.