

Support Information

Cobalt (II) terpyridine complexes: synthesis, characterization, antiproliferative activity and molecular docking with proteins and DNA

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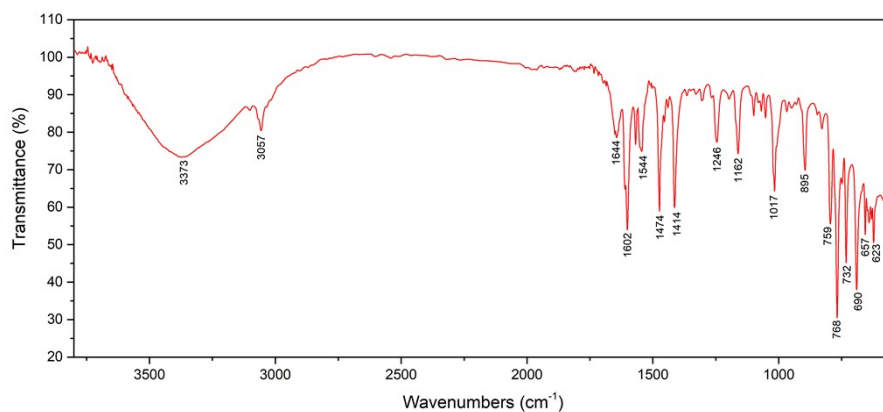


Figure S1. The IR diagram of complex $[\text{Co}(\text{L}^1)_2]\text{Cl}_2$ (**1**)

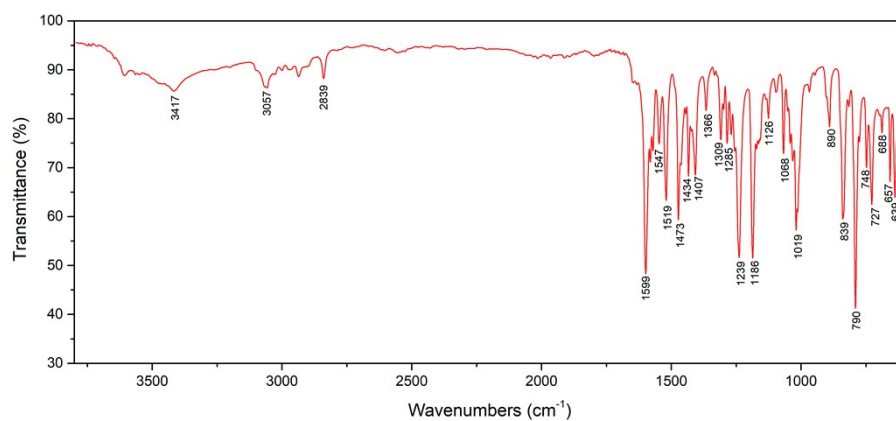


Figure S2. The IR diagram of complex $[\text{Co}(\text{L}^2)_2]\text{Cl}_2$ (**2**)

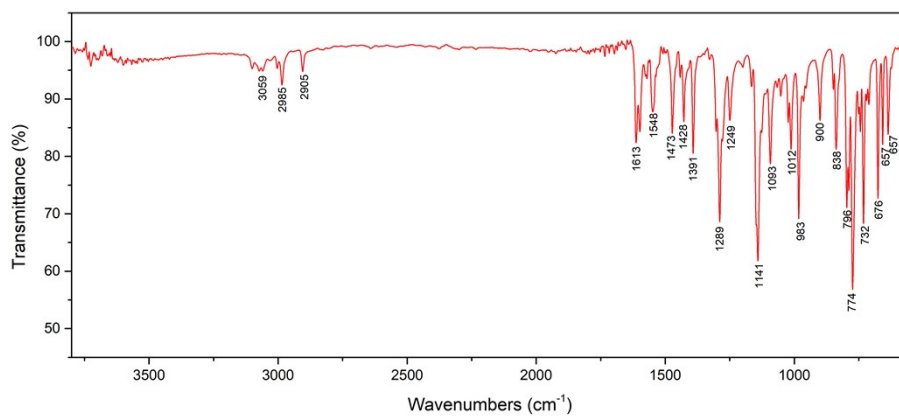


Figure S3. The IR diagram of complex $[\text{Co}(\text{L}^3)_2]\text{Cl}_2$ (**3**)

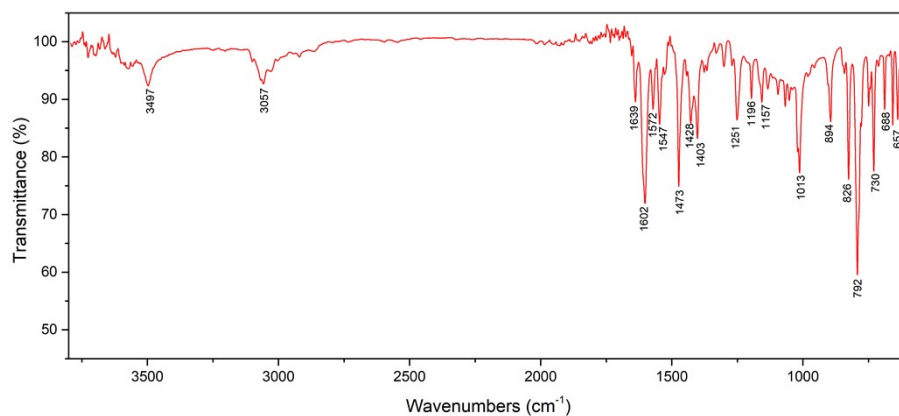


Figure S4. The IR diagram of complex $[\text{Co}(\text{L}^4)_2]\text{Cl}_2$ (**4**)

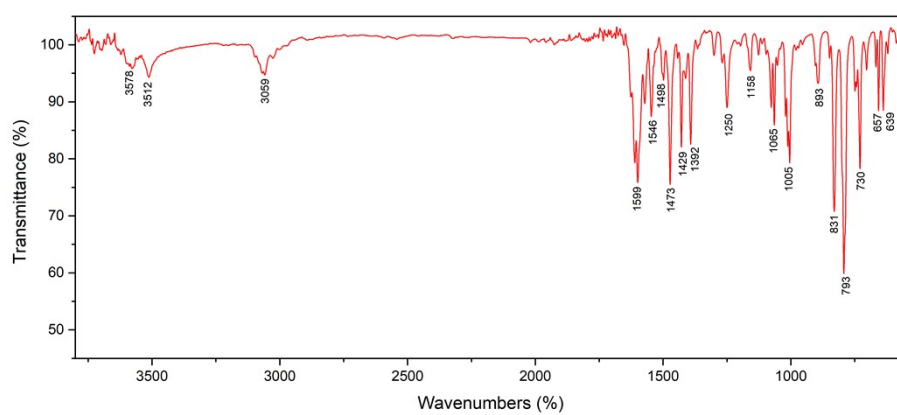


Figure S5. The IR diagram of complex $[\text{Co}(\text{L}^5)_2]\text{Cl}_2$ (**5**)

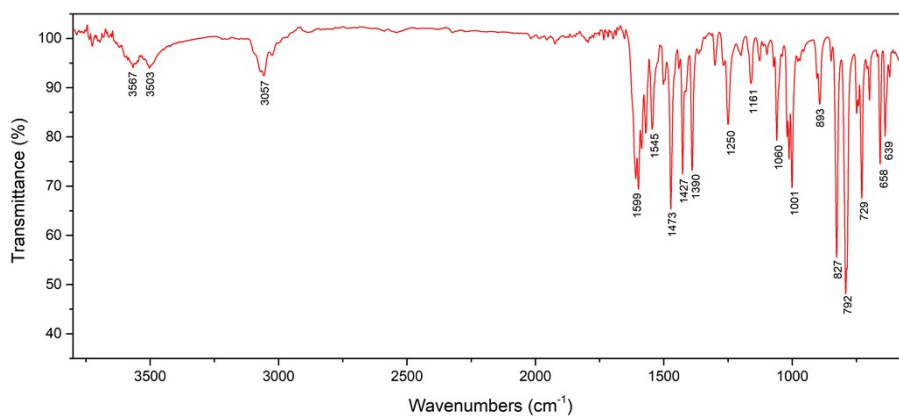


Figure S6. The IR diagram of complex $[\text{Co}(\text{L}^6)_2]\text{Cl}_2$ (**6**)

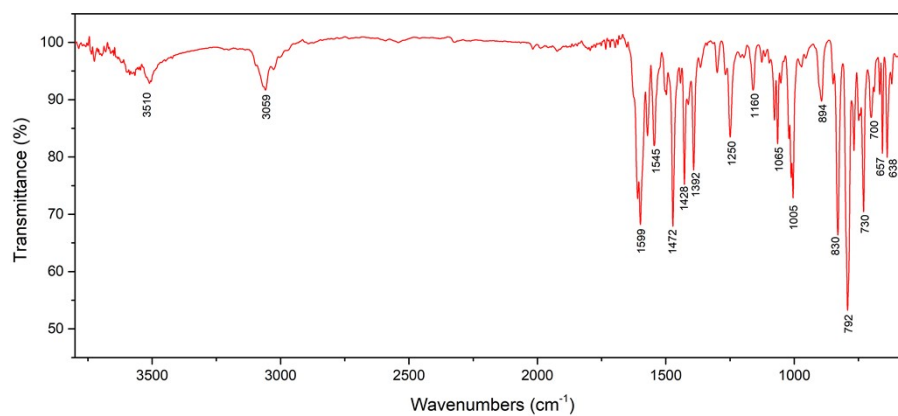


Figure S7. The IR diagram of complex $[\text{Co}(\text{L}^7)_2]\text{Cl}_2$ (**7**)

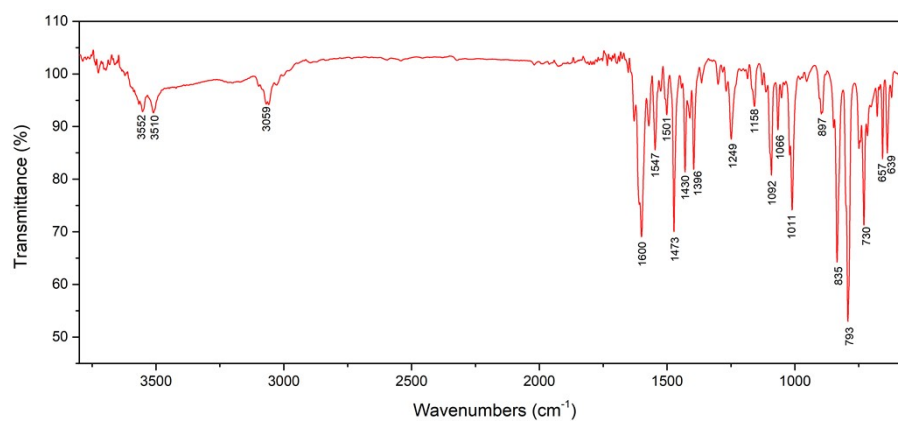


Figure S8. The IR diagram of complex $[\text{Co}(\text{L}^8)_2]\text{Cl}_2$ (**8**)

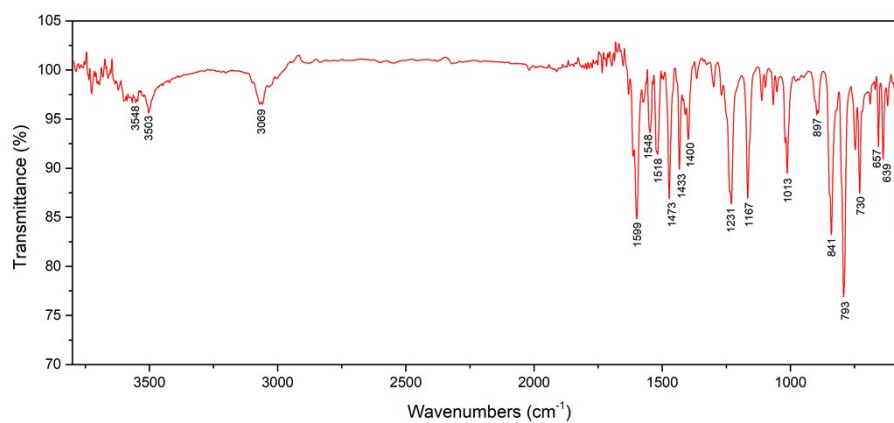


Figure S9. The IR diagram of complex $[\text{Co}(\text{L}^9)_2]\text{Cl}_2$ (**9**)

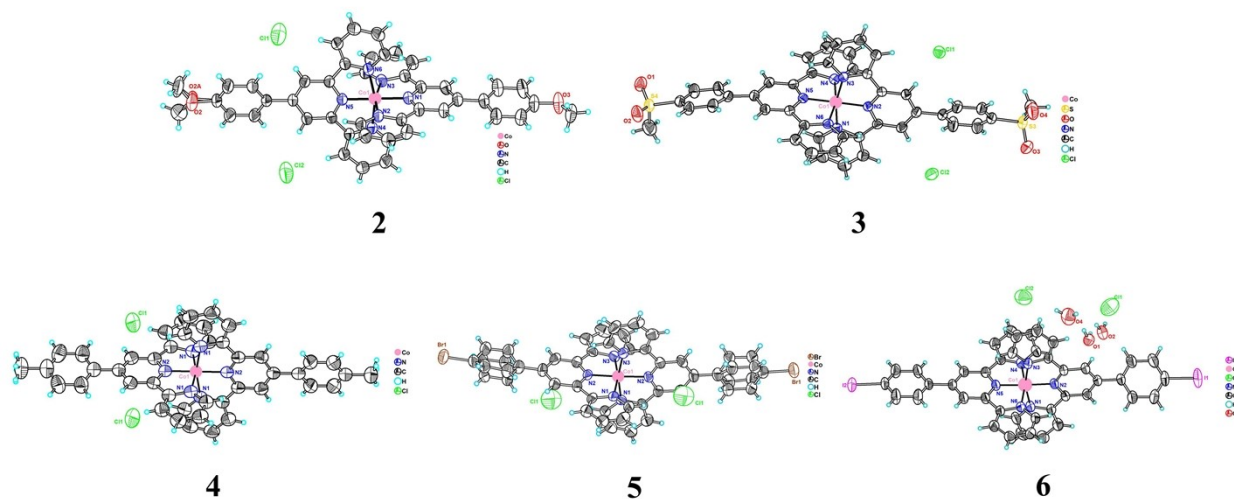


Figure S10. The crystallographic structure diagram of complexes 2-6.

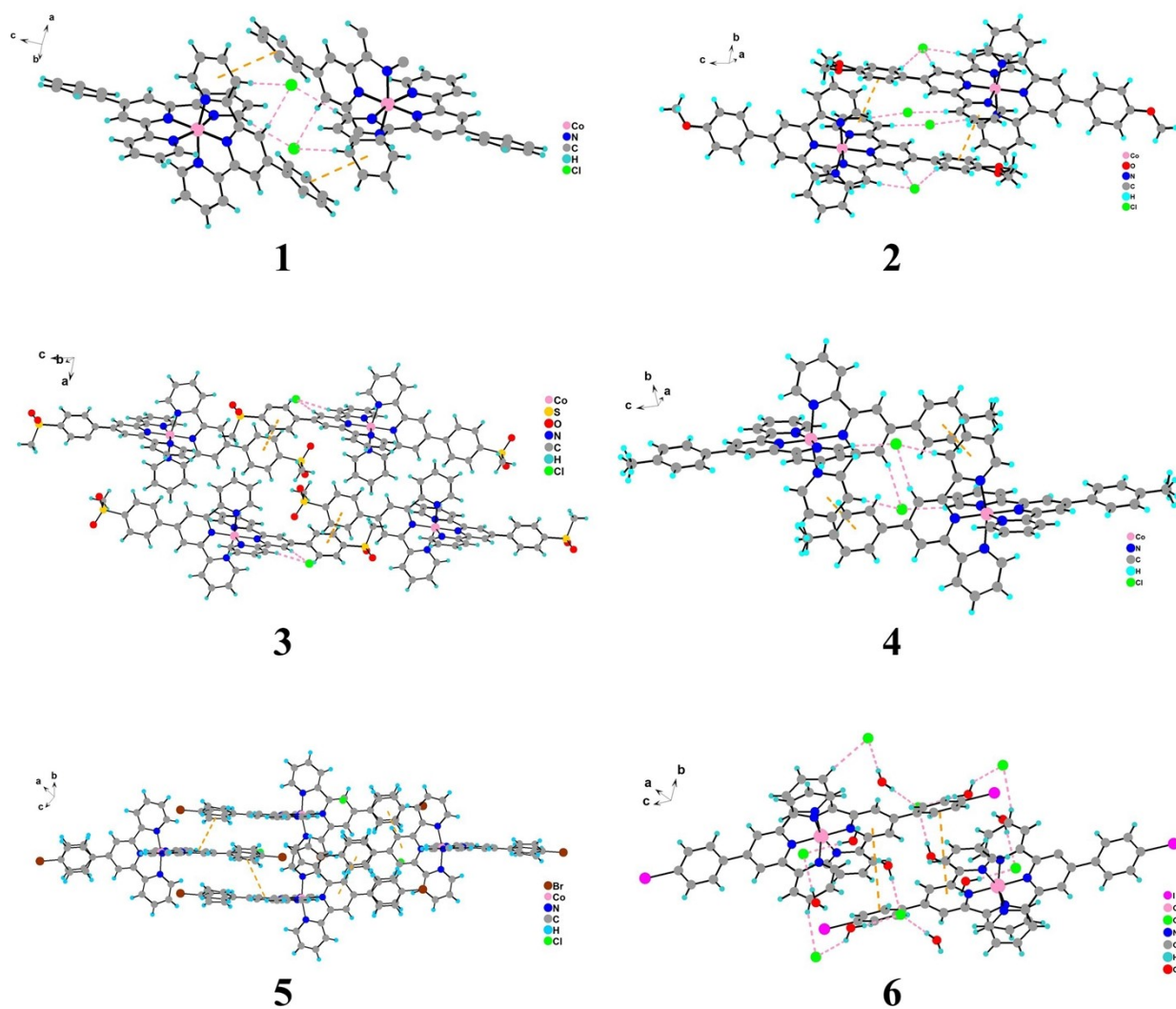


Figure S11. The packing diagram of complex 1-6.

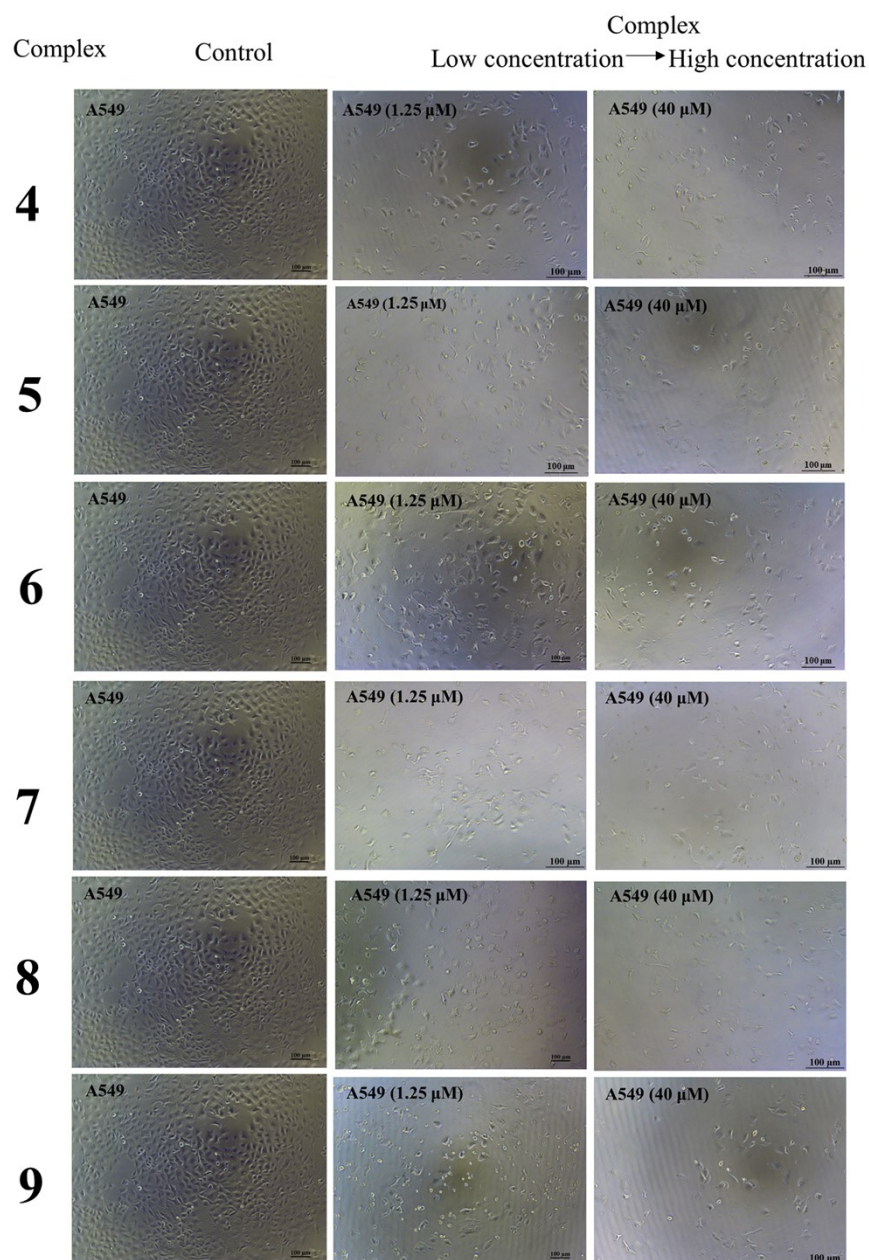


Figure S12. The microscopic images of A549 cells treated with increased concentrations of complexes **4-9**.

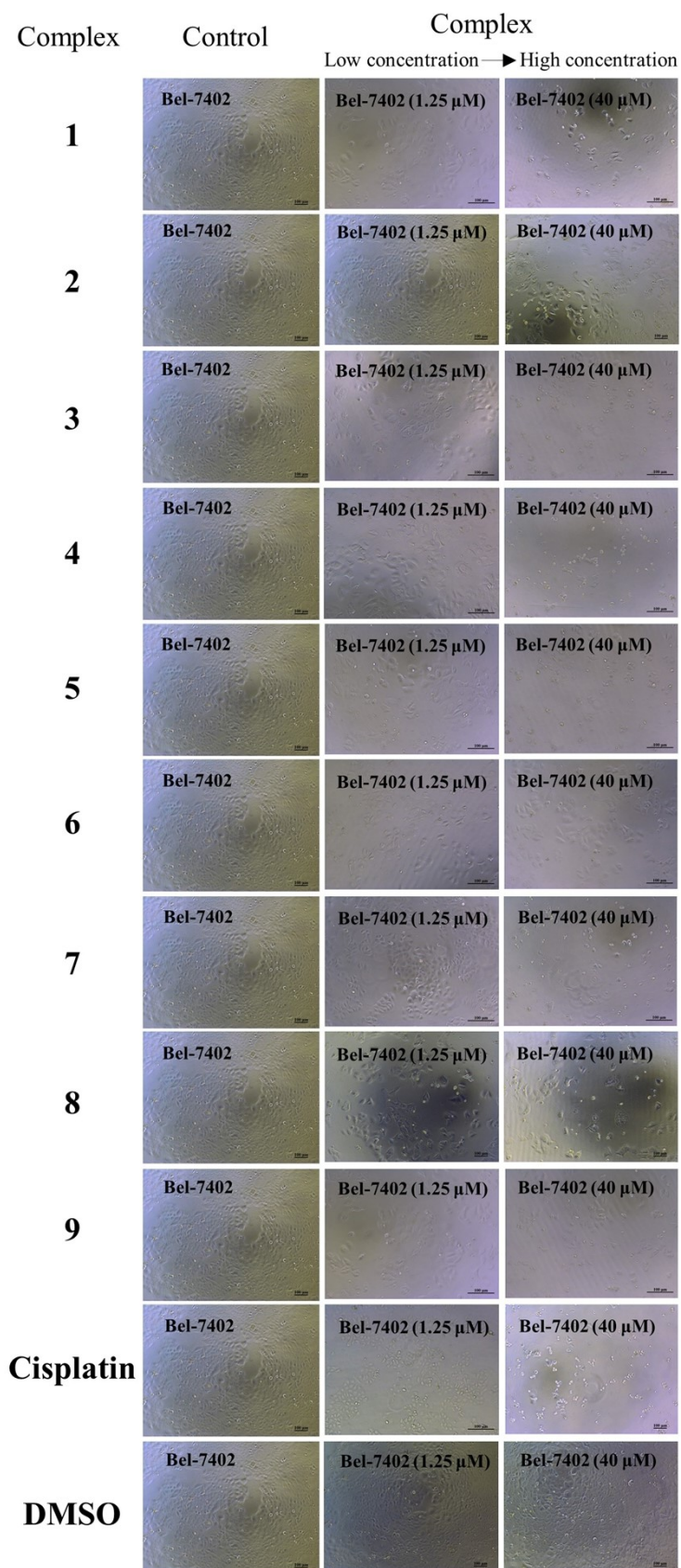


Figure S13. The microscopic images of Bel-7402 cells treated with increased concentrations of complexes **1-9**, cisplatin and DMSO.

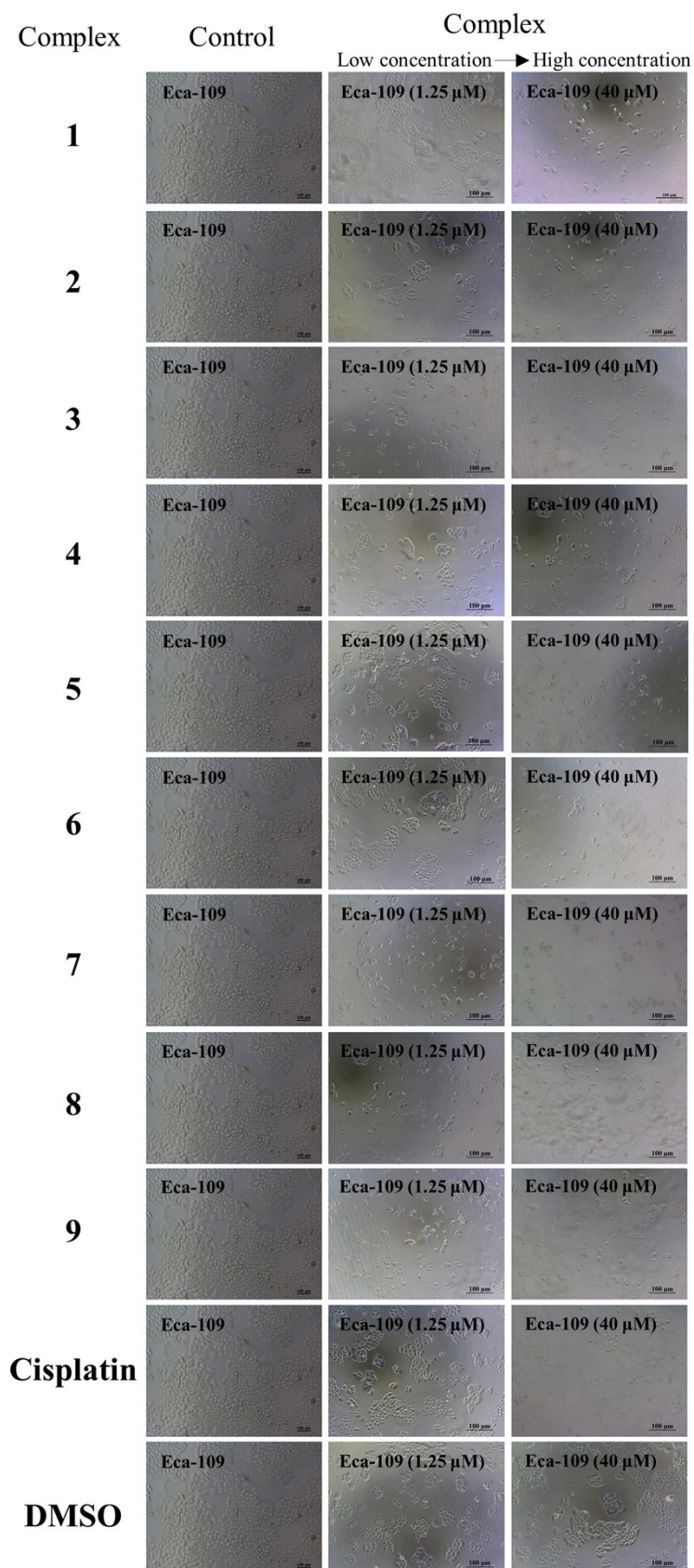


Figure S14. The microscopic images of Eca-109 cells treated with increased concentrations of complexes 1-9, cisplatin and DMSO.

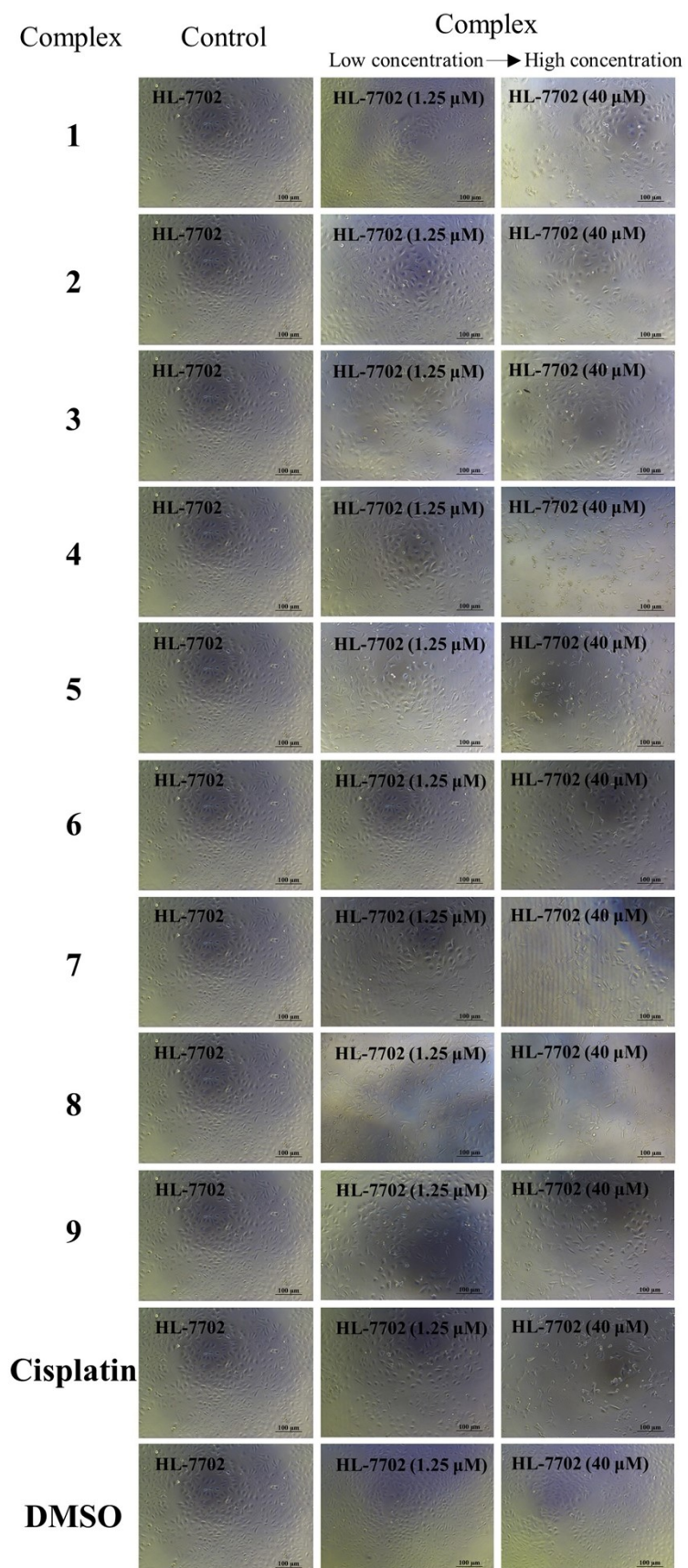


Figure S15. The microscopic images of HL-7702 cells treated with increased concentrations of complexes **1-9**, cisplatin and DMSO.

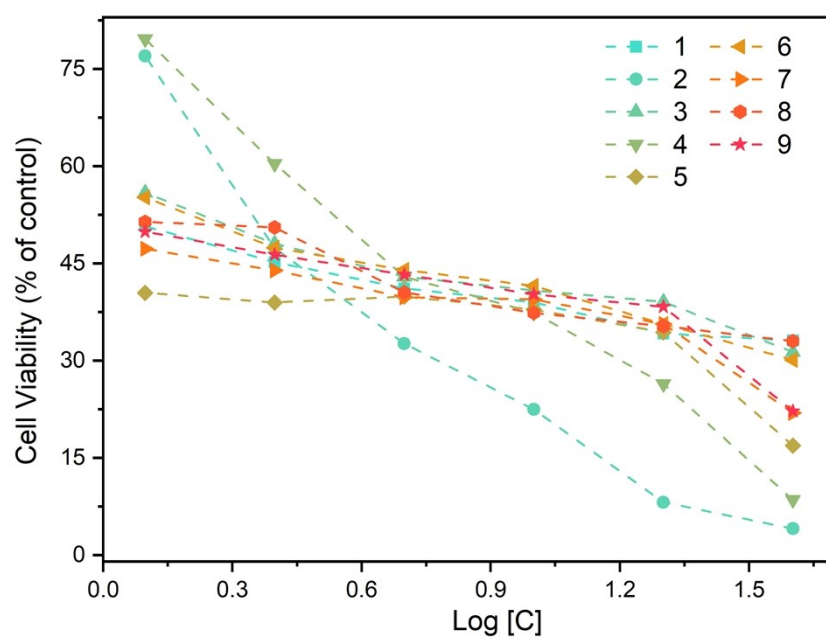


Figure S16. The curves of the cell viability vs. the concentration of complexes **1-9** against Bel-7402 cell line.

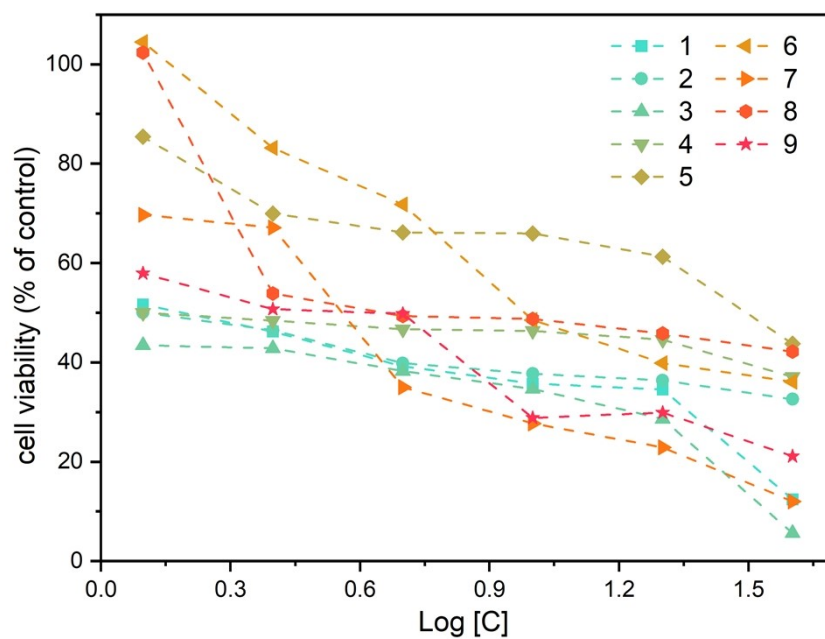


Figure S17. The curves of the cell viability vs. the concentration of complexes **1-9** against Eca-109 cell line.

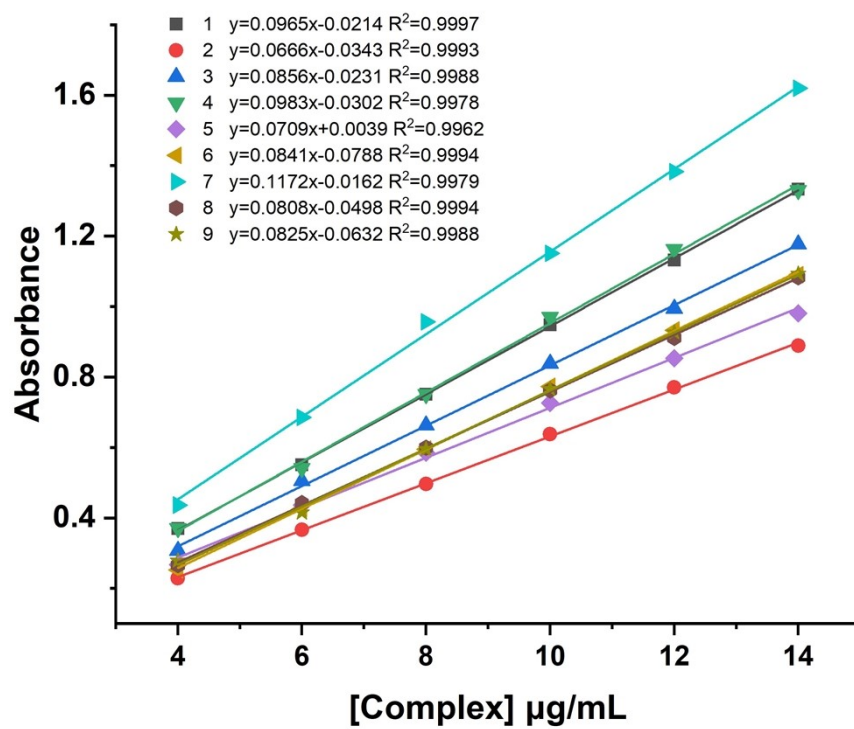


Figure S18. The standard curves of UV-Vis spectra for complexes 1-9.

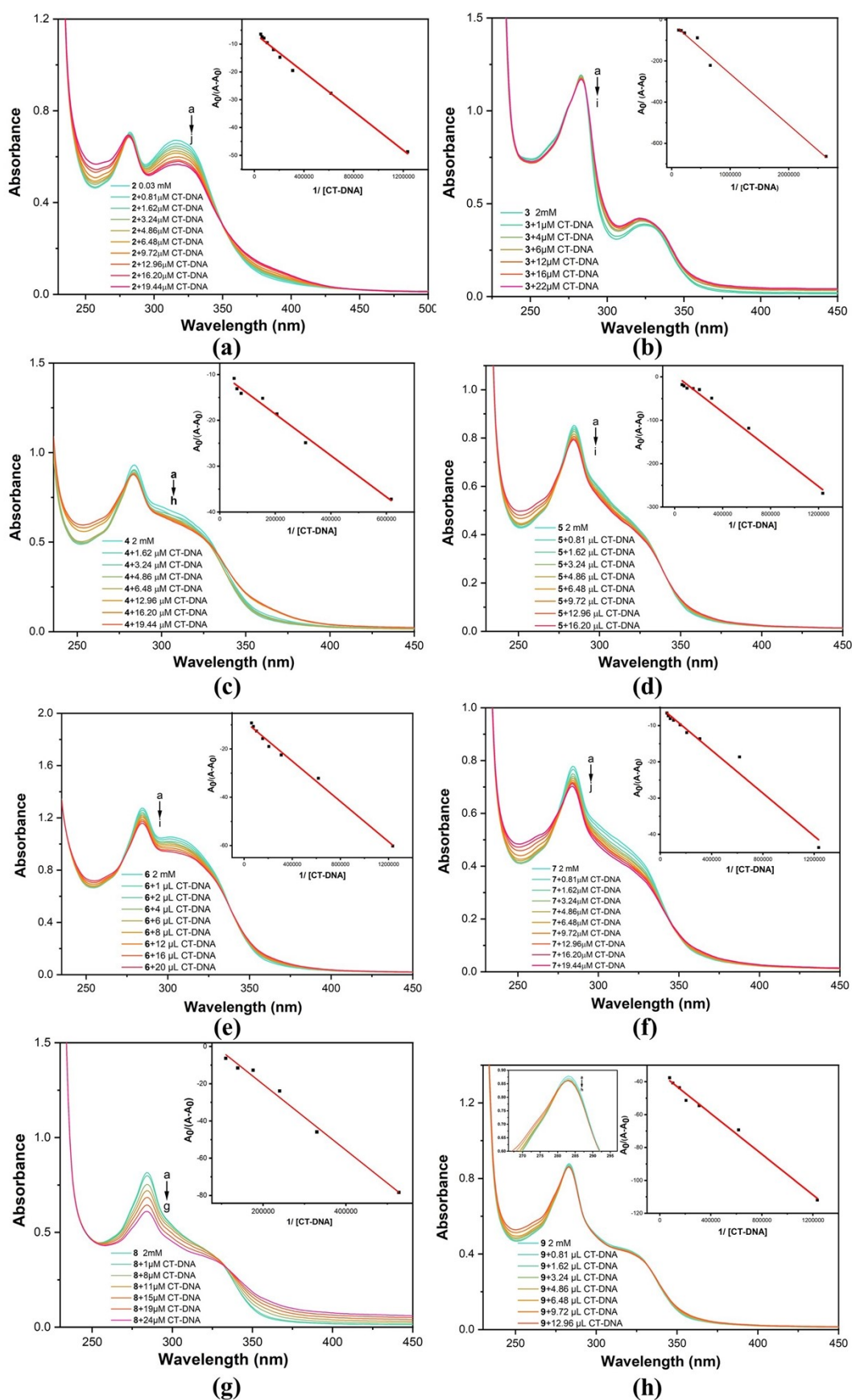


Figure S19. UV-vis spectra of complexes 2-9 (a-h) in the different concentrations of CT-DNA in Tris-HCl 1.0×10^{-3} (pH 7.2).

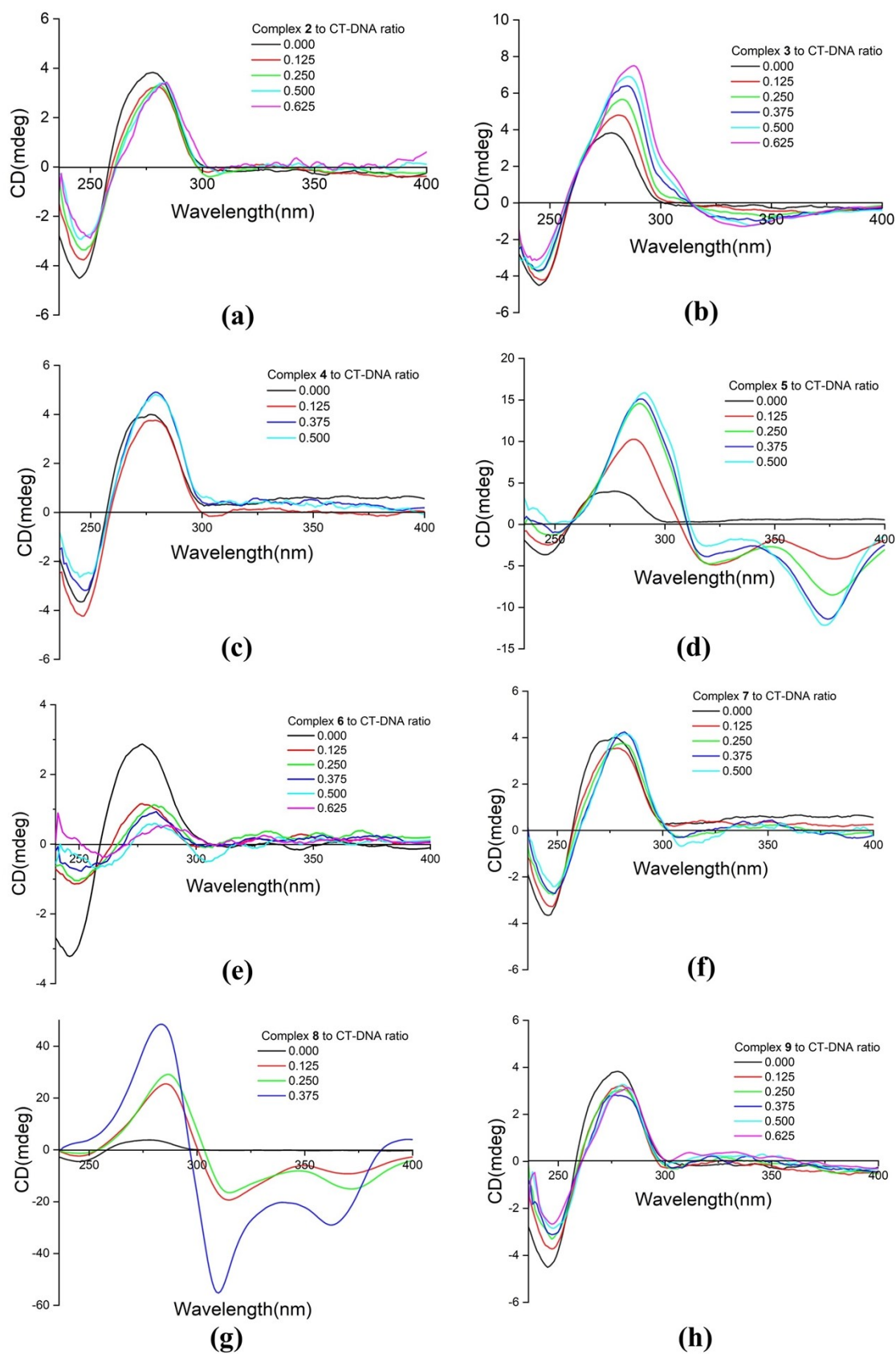


Figure S20. CD spectra of CT-DNA in the presence of complexes 2-9.

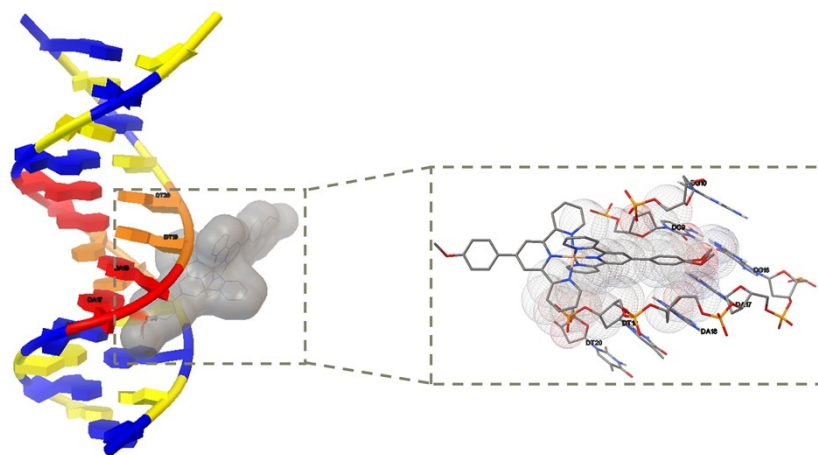


Figure S21. View of the energy minimized docked poses of complex **2** with B-DNA (PDB ID: 1BNA).

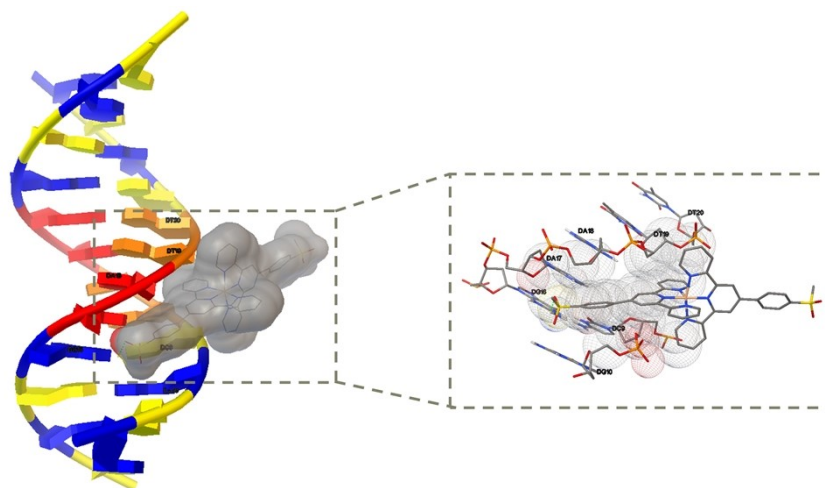


Figure S22. View of the energy minimized docked poses of complex **3** with B-DNA (PDB ID: 1BNA).

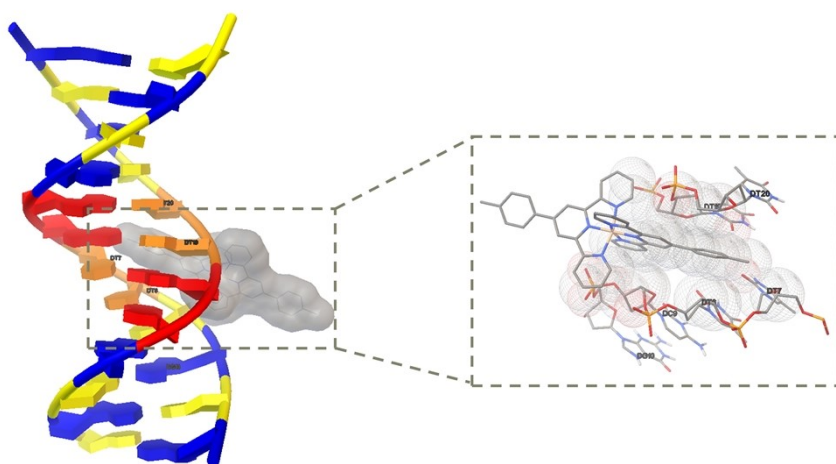


Figure S23. View of the energy minimized docked poses of complex **4** with B-DNA (PDB ID: 1BNA).

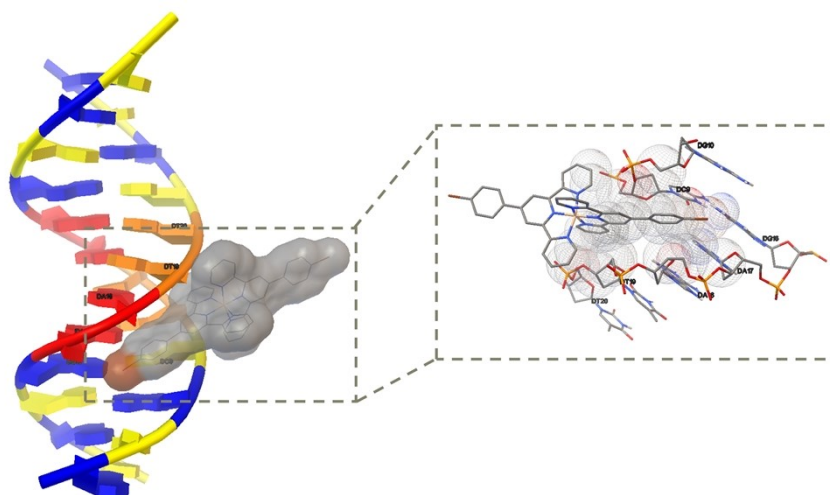


Figure S24. View of the energy minimized docked poses of complex **5** with B-DNA (PDB ID: 1BNA).

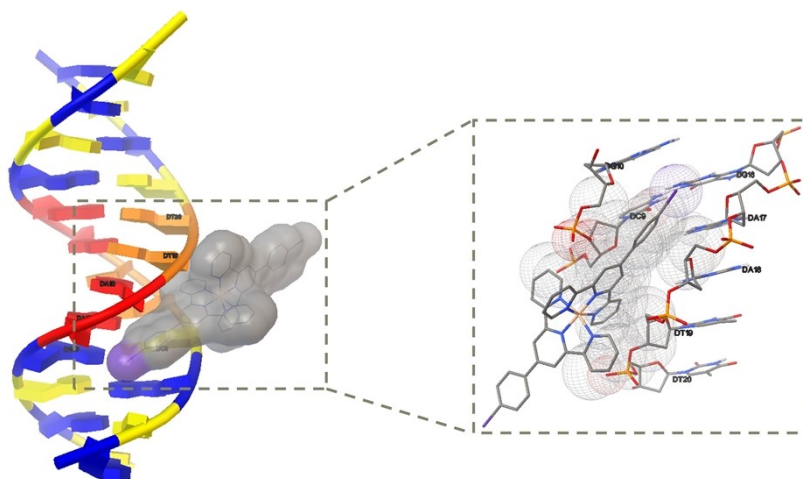


Figure S25. View of the energy minimized docked poses of complex **6** with B-DNA (PDB ID: 1BNA).

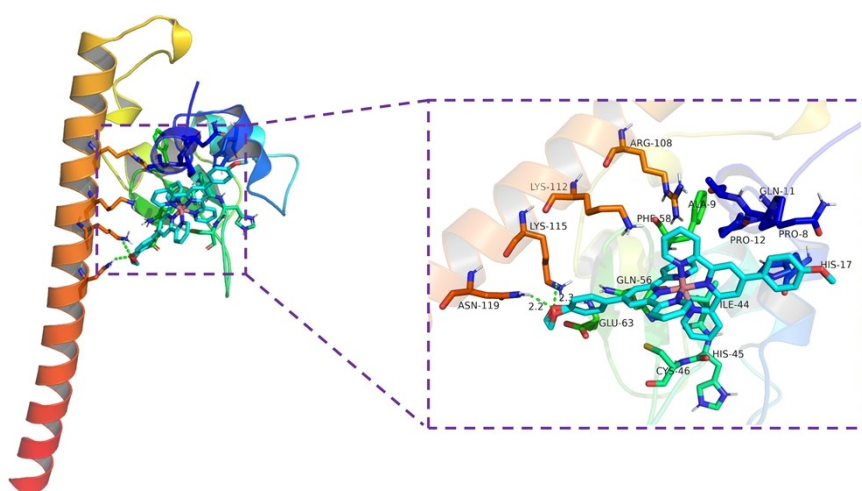


Figure S26. Binding modes of complex **2** with survivin protein (PDB ID: 3UIH).

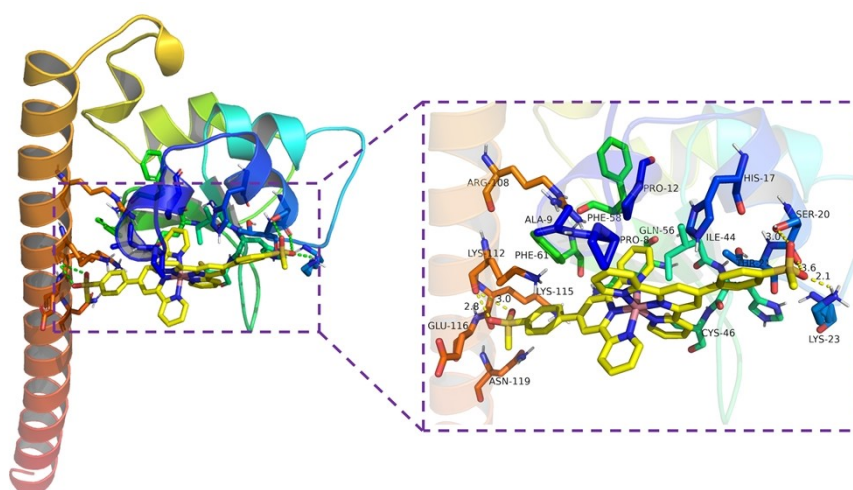


Figure S27. Binding modes of complex **3** with survivin protein (PDB ID: 3UIH).

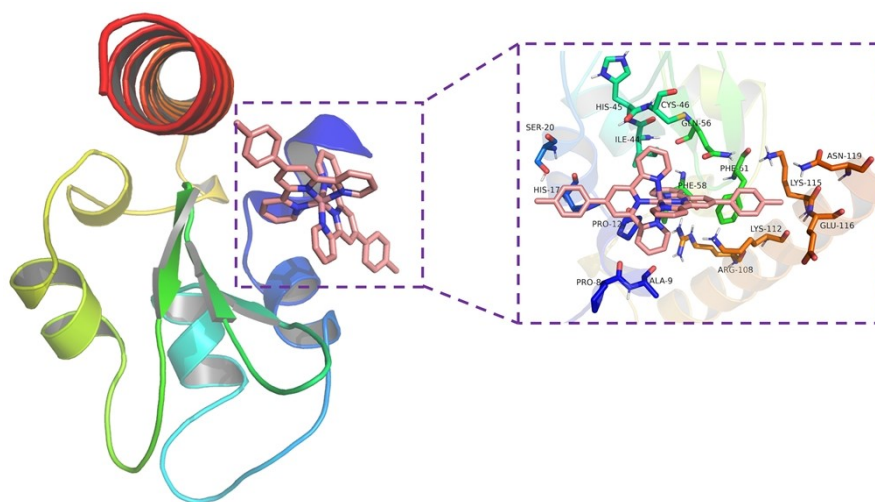


Figure S28. Binding modes of complex **4** with survivin protein (PDB ID: 3UIH).

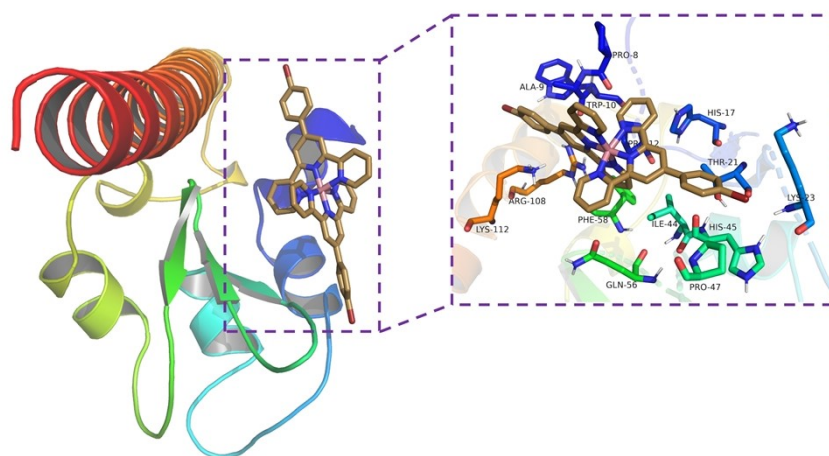


Figure S29. Binding modes of complex **5** with survivin protein (PDB ID: 3UIH).

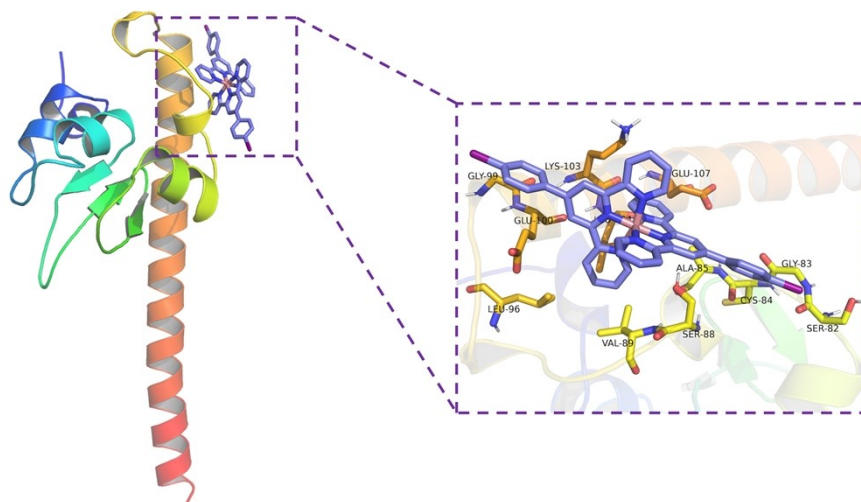


Figure S30. Binding modes of complex **6** with survivin protein (PDB ID: 3UIH).

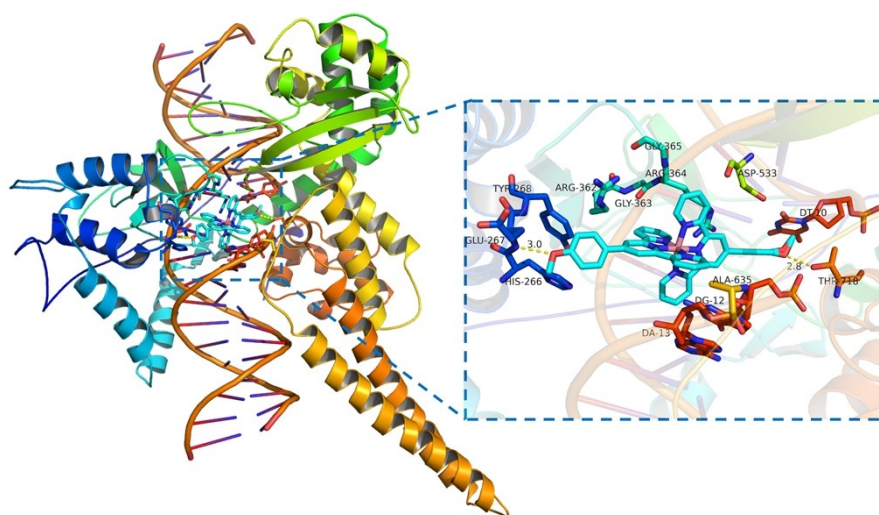


Figure S31. Binding modes of complex **2** with Top I (PDB ID: 1T8I).

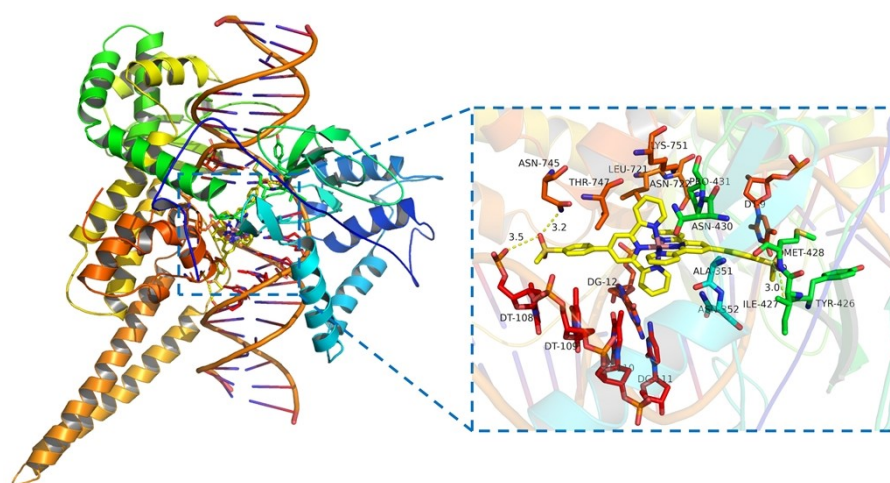


Figure S32. Binding modes of complex **3** with Top I (PDB ID: 1T8I).

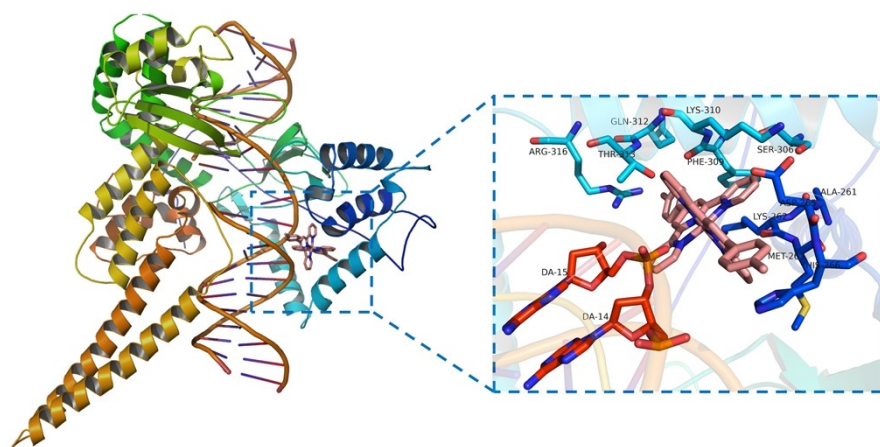


Figure S33. Binding modes of complex **4** with Top I (PDB ID: 1T8I).

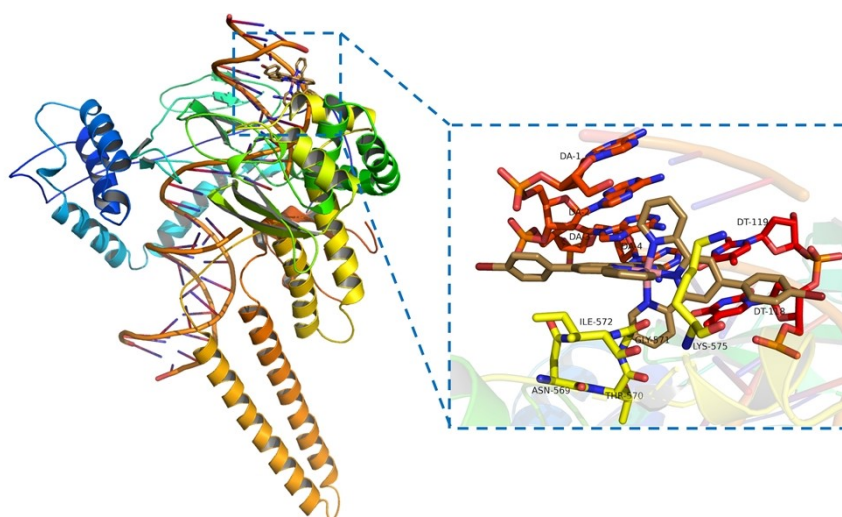


Figure S34. Binding modes of complex **5** with Top I (PDB ID: 1T8I).

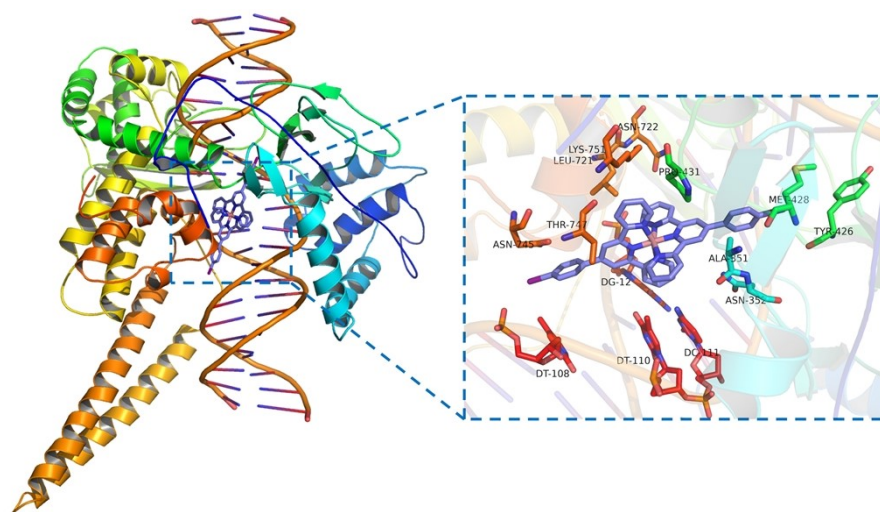


Figure S35. Binding modes of complex **6** with Top I (PDB ID: 1T8I).

Table S1. Selected geometric parameters of the complexes.

Complex	1	2	3	4	5	6
Empirical formula	C ₄₂ H ₃₀ Cl ₂ CoN ₆	C ₄₄ H ₃₄ Cl ₂ CoN ₆ O ₂	C ₄₄ H ₃₄ Cl ₂ CoN ₆ O ₄ S	C ₄₄ H ₃₄ Cl ₂ CoN ₆	C ₄₂ H ₂₈ Br ₂ Cl ₂ CoN ₆	C ₄₂ H ₃₁ Cl ₂ CoI ₂ N ₆ O ₃
Formula weight	748.55	808.6	904.72	776.6	906.35	1051.36
Temperature	296(2) K	296(2) K	296(2) K	296(2) K	296(2)	298 K
Crystal system	Triclinic	Triclinic	Triclinic	Tetragonal	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$I4_1/a$	$C2/c$	$C2/c$
<i>a</i> (Å)	10.6413(7)	10.725(2)	11.5679(4)	11.4940(5)	24.649(4)	16.5178(9)
<i>b</i> (Å)	11.5087(6)	11.525(2)	14.3215(5)	11.4940(5)	9.6058(17)	14.7305(9)
<i>c</i> (Å)	19.8685(11)	19.766(4)	15.9903(6)	35.533(4)	23.874(3)	37.360(2)
α (°)	97.120(4)	106.16(3)	73.603(3)	90	90°	90
β (°)	95.761(5)	94.85(3)	76.313(3)	90	118.391(19)°	92.850(5)
γ (°)	111.838(6)	97.02(3)	77.065(3)	90	90°	90
Volume (Å ³)	2212.7(2)	2311.0(9)	2433.90(16)	4694.3(6)	4973.0(16)	9079.1(9)
<i>Z</i>	2	2	2	4	4	8
Density (calculated) (Mg/m ³)	1.124	1.162	1.235	1.099	1.211	1.538
Absorption coefficient (mm ⁻¹)	0.541	0.526	0.592	0.512	2.090	1.898
<i>F</i> (000)	770	834	930	1604	1812	4128
Crystal size (mm ³)	0.15 × 0.11 × 0.1	0.11 × 0.07 × 0.06	0.1 × 0.07 × 0.07	0.1 × 0.07 × 0.05	0.14 × 0.12 × 0.12	0.2 × 0.13 × 0.12
θ_{\max} , θ_{\min} (°)	3.053, 29.494	2.877, 29.525	2.756, 29.419°	3.398, 29.488°	1.878, 29.328°	3.249, 29.420°
Index range <i>h</i> , <i>k</i> , <i>l</i>	-13 ≤ <i>h</i> ≤ 9 -14 ≤ <i>k</i> ≤ 13 -27 ≤ <i>l</i> ≤ 26	-13 ≤ <i>h</i> ≤ 10 -14 ≤ <i>k</i> ≤ 13 -27 ≤ <i>l</i> ≤ 25	-15 ≤ <i>h</i> ≤ 15 -19 ≤ <i>k</i> ≤ 15 -21 ≤ <i>l</i> ≤ 21	-9 ≤ <i>h</i> ≤ 15 -9 ≤ <i>k</i> ≤ 15 -48 ≤ <i>l</i> ≤ 46	-32 ≤ <i>h</i> ≤ 28 -13 ≤ <i>k</i> ≤ 12 -20 ≤ <i>l</i> ≤ 32	-22 ≤ <i>h</i> ≤ 20 -20 ≤ <i>k</i> ≤ 19 -48 ≤ <i>l</i> ≤ 39
Reflections collected/unique	20797	24031	27736	12160	12236	25664
Data/restraints/parameters	10239 / 0 / 460	10726 / 50 / 518	11431 / 0 / 534	2882 / 0 / 127	5700 / 159 / 277	10781 / 0 / 481
Goodness-of-fit on <i>F</i> ²	1.036	1.06	1.037	1.058	0.980	1.024
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0672 w <i>R</i> 2 = 0.2052	<i>R</i> 1 = 0.0647 w <i>R</i> 2 = 0.1942	<i>R</i> 1 = 0.0442 w <i>R</i> 2 = 0.1289	<i>R</i> 1 = 0.0695 w <i>R</i> 2 = 0.2129	<i>R</i> 1 = 0.0793 w <i>R</i> 2 = 0.2111	<i>R</i> 1 = 0.0638 w <i>R</i> 2 = 0.1677
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0825 w <i>R</i> 2 = 0.2232	<i>R</i> 1 = 0.0812 w <i>R</i> 2 = 0.2147	<i>R</i> 1 = 0.0550 w <i>R</i> 2 = 0.1376	<i>R</i> 1 = 0.0945 w <i>R</i> 2 = 0.2407	<i>R</i> 1 = 0.1635 w <i>R</i> 2 = 0.2595	<i>R</i> 1 = 0.0819 w <i>R</i> 2 = 0.1851
Largest diff. peak and hole (e Å ⁻³)	0.559 and -1.062	0.855 and -1.029	1.067 and -0.515	0.915 and -0.296	0.467 and -0.468	1.382 and -1.646

Table S2. Distribution coefficients of complexes **1-9**

Complex	Absorbance			C _{organic} (µg/mL)			Log D _{7.4}
	1	2	3	1	2	3	Average
1	0.950	0.948	0.946	10.07	10.05	10.02	0.612
2	0.637	0.638	0.639	10.08	10.09	10.11	0.623
3	0.837	0.838	0.839	10.05	10.06	10.07	0.615
4	0.970	0.970	0.969	10.17	10.17	10.16	0.639
5	0.728	0.727	0.725	10.21	10.20	10.17	0.645
6	0.774	0.773	0.773	10.14	10.13	10.13	0.632
7	1.151	1.150	1.152	9.96	9.95	9.97	0.593
8	0.764	0.762	0.761	10.07	10.05	10.03	0.613
9	0.767	0.766	0.765	10.06	10.05	10.04	0.613

Table S3. Hydrogen bond interactions for compounds **2, 3**.

Compound	Receptor	Bonds formed	Bond distance (Å)
2	B-DNA (1BNA)	O...H-N(DA-17)	2.2
	B-DNA (1BNA)	O...H-N(DG-16)	2.8
	survivin (3UIH)	O...H-N(ASN-119)	2.2
	survivin (3UIH)	O...H-N(LYS-115)	2.3
	DNA-topoisomerase I (1T8I)	O-H...O (DLU-267)	3.0
	DNA-topoisomerase I (1T8I)	O...H-N()	2.8
3	B-DNA (1BNA)	O-H...O2 (DA-17)	2.6
	B-DNA (1BNA)	O2...H-N(DA-17)	2.5
	B-DNA (1BNA)	O-H...O1 (DG-16)	2.1
	survivin (3UIH)	O-H...O1 (LYS-112)	2.8
	survivin (3UIH)	O-H...O2 (LYS-112)	3.0
	survivin (3UIH)	O-H...O3 (SER-20)	3.0
	survivin (3UIH)	O-H...O4 (SER-20)	3.6
	survivin (3UIH)	O...H-N(LYS-23)	2.1
	DNA-topoisomerase I (1T8I)	O-H...O2 (DT-108)	3.5
	DNA-topoisomerase I (1T8I)	O-H...O2 (ANS-745)	3.2
	DNA-topoisomerase I (1T8I)	O-H...O4 (TYR-426)	3.0
	DNA-topoisomerase I (1T8I)	O...H-N(MET-428)	3.0

Synthesis of complexes 1-9

4'-(substituted phenyl)-terpyridine ligands **L¹-L⁹** were synthesized from each of the 4-substituted benzaldehyde and 2-acetylpyridine according to the literature. Complexes **1-9** were synthesized by the reaction of **L¹-L⁹** with CoCl₂·6H₂O added in stoichiometric amounts, respectively, in a methanol-CH₂Cl₂ solution.

[Co(L¹)₂]Cl₂ (1). A solution of CoCl₂·6H₂O (0.12 g, 0.48 mmol) in ethanol (10 mL) was added dropwise to a 10 mL dichloromethane solution of **L¹** (0.10 g, 0.32 mmol) in a 50 mL flask, and stirred for 8 h at ambient temperature. A brown solid (0.075 g, 75% yield based on **L¹**) was obtained upon filtration of the solution and washed with dichloromethane and dried in a desiccator. Anal. Calcd for C₄₂H₃₀N₆CoCl₂·3.75 CH₂Cl₂·2.1H₂O: C, 49.73; H, 3.80; N, 7.60%. Found: C, 49.25; H, 3.36; N, 8.16 %. IR (KBr disc) (cm⁻¹) (s = strong, m = medium, w = weak): 3057 (m, *ν*_{C-H}), 1644 (m, *n*-pyridyl-H), 1602 (s), 1544 (m, *n*-pyridyl-H), 1474 (s, *n*-pyridyl-H), 1414 (s), 1246 (s, *β*_{C-H}), 1162 (s, *β*_{C-H}), 1017 (s, *β*_{C-H}), 895 (m, *γ*_{C-H}), 759 (m, *γ*_{C-H}), 768 (s, *γ*_{C-H}), 732 (m, *γ*_{C-H}), 690 (m, *γ*_{C-H}), 657 (m), 623 (m).

[Co(L²)₂]Cl₂ (2). A solution of CoCl₂·6H₂O (0.11 g, 0.44 mmol) in ethanol (10 mL) was added dropwise to a solution of **L²** (0.10 g, 0.29 mmol) dissolved in dichloromethane (10 mL) in a 50 mL flask and stirred for 8 h at ambient temperature. A brown solid (0.067 g, 67% yield based on **L²**) was obtained upon filtration of the solution and washed with dichloromethane and dried in a desiccator. Anal. Calcd for C₄₄H₃₄N₆O₂CoCl₂·2.1CH₂Cl₂: C, 56.10; H, 3.90; N, 8.51%. Found: C, 55.72; H, 4.12; N, 8.70 %. IR (KBr disc) (cm⁻¹): 3057 (m, *ν*_{C-H}), 2839 (w, *ν*_{C-H}), 1599 (s, *n*-pyridyl-H), 1547 (w, *n*-pyridyl-H), 1519 (s, *n*-pyridyl-H), 1473 (s, *ν*_{C=C}), 1434 (m, *ν*_{C=C}), 1407 (m, *ν*_{C=C}), 1366 (w, *ν*_{C=C}), 1239 (s, *ν*_{Ar-O-Me}), 1183 (s, *ν*_{Ar-O-Me}), 1126 (w, *β*_{C-H}), 1068 (m, *β*_{C-H}), 1019 (s, *β*_{C-H}), 890 (w, *γ*_{C-H}), 839 (s, *γ*_{C-H}), 790 (s, *γ*_{C-H}), 748 (m, *γ*_{C-H}), 727 (s, *γ*_{C-H}), 657 (m), 639 (s).

[Co(L³)₂]Cl₂ (3). A solution of CoCl₂·6H₂O (0.09 g, 0.38 mmol) in ethanol (10 mL) was added dropwise to a solution of **L³** (0.10 g, 0.29 mmol) dissolved in dichloromethane (10 mL) in a 50 mL flask and stirred for 8 h at ambient temperature. A brown solid (0.071 g, 71% yield based on **L³**) was obtained upon filtration of the solution and washed with dichloromethane and dried in a desiccator. Anal. Calcd for C₄₄H₃₄N₆O₄S₂CoCl₂·CH₂Cl₂: C, 54.61; H, 3.66; N, 8.49%. Found: C, 54.44; H, 3.20; N, 8.65 %. IR (KBr disc) (cm⁻¹): 3059 (w, *ν*_{C-H}), 2985 (w, *ν*_{C-H}), 2905 (w, *ν*_{C-H}), 1613 (s, *n*-pyridyl-H), 1548 (m, *n*-pyridyl-H), 1473 (s, *ν*_{C=C}), 1428 (s, *ν*_{C=C}), 1391 (s, *ν*_{C=C}), 1289 (s, *ν*_{SO2}), 1249 (w, *ν*_{SO2}), 1141 (s, *ν*_{SO2}), 1093 (m, *β*_{C-H}), 1012 (m, *β*_{C-H}), 983 (s, *γ*_{C-H}), 900 (w, *γ*_{C-H}), 838 (m, *γ*_{C-H}), 796 (m, *ν*_{S-O}), 774 (s, *γ*_{C-H}), 732 (s, *γ*_{C-H}), 676 (m), 657 (m), 636 (m).

[Co(L⁴)₂]Cl₂ (4). A solution of CoCl₂·6H₂O (0.11 g, 0.46 mmol) in ethanol (10 mL) was added dropwise to a solution of **L⁴** (0.10 g, 0.31 mmol) dissolved in dichloromethane (10 mL) in a 50 mL flask and stirred for 8 h at ambient temperature. A brown solid (0.065 g, 65% yield based on **L⁴**)

was obtained upon filtration of the solution and washed with dichloromethane and dried in a desiccator. IR (KBr disc) (cm^{-1}): 3057 (w, $\nu_{\text{C-H}}$), 3022 (w, $\nu_{\text{C-H}}$), 2918 (w, $\nu_{\text{C-H}}$), 2864 (w, $\nu_{\text{C-H}}$), 1602 (s, *n*-pyridyl-H), 1547 (m, *n*-pyridyl-H), 1473 (s, $\nu_{\text{C=C}}$), 1428 (m, $\nu_{\text{C=C}}$), 1403 (s, $\nu_{\text{C=C}}$), 1251 (m, $\beta_{\text{C-H}}$), 1013 (m, $\beta_{\text{C-H}}$), 894 (w, $\gamma_{\text{C-H}}$), 826 (m, $\gamma_{\text{C-H}}$), 792 (s, $\gamma_{\text{C-H}}$), 730 (s, $\gamma_{\text{C-H}}$), 688 (w), 657 (m). **[Co(L⁵)₂]Cl₂ (5).** A solution of CoCl₂·6H₂O (0.09 g, 0.39 mmol) in ethanol (10 mL) was added dropwise to a solution of L⁵ (0.10 g, 0.26 mmol) dissolved in dichloromethane (10 mL) in a 50 mL flask and stirred for 8 h at ambient temperature. A brown solid (0.072 g, 72% yield based on L⁵) was obtained upon filtration of the solution and washed with dichloromethane and dried in a desiccator. Anal. Calcd for C₄₂H₂₈Br₂N₆CoCl₂·2.2CH₂Cl₂·0.2H₂O: C, 48.40; H, 3.01; N, 7.66%. Found: C, 47.96; H, 2.52; N, 8.06 %. IR (KBr disc) (cm^{-1}): 3057 (w, $\nu_{\text{C-H}}$), 1599 (s, *n*-pyridyl-H), 1545 (m, *n*-pyridyl-H), 1473 (s, $\nu_{\text{C=C}}$), 1427 (m, $\nu_{\text{C=C}}$), 1390 (m, $\nu_{\text{C=C}}$), 1250 (m, $\beta_{\text{C-H}}$), 1161 (w, $\beta_{\text{C-H}}$), 1060 (m, $\beta_{\text{C-H}}$), 1001 (s, $\beta_{\text{C-H}}$), 893 (w, $\gamma_{\text{C-H}}$), 827 (s, $\gamma_{\text{C-H}}$), 792 (s, $\gamma_{\text{C-H}}$), 729 (m, $\gamma_{\text{C-H}}$), 658 (m, $\nu_{\text{C-Br}}$), 639 (m).

[Co(L⁶)₂]Cl₂ (6). A solution of CoCl₂·6H₂O (0.08 g, 0.34 mmol) in ethanol (10 mL) was added dropwise to a solution of L⁶ (0.10 g, 0.23 mmol) dissolved in dichloromethane (10 mL) in a 50 mL flask and stirred for 8 h at ambient temperature. A brown solid (0.069 g, 69% yield based on L⁶) was obtained upon filtration of the solution and washed with dichloromethane and dried in a desiccator. Anal. Calcd for C₄₂H₂₈I₂N₆CoCl₂·2.1CH₂Cl₂·1.8H₂O: C, 43.73; H, 2.98; N, 6.94%. Found: C, 43.49; H, 2.97; N, 7.27 %. IR (KBr disc) (cm^{-1}): 3059 (w, $\nu_{\text{C-H}}$), 1599 (s, *n*-pyridyl-H), 1546 (m, *n*-pyridyl-H), 1473 (s, $\nu_{\text{C=C}}$), 1429 (m, $\nu_{\text{C=C}}$), 1392 (m, $\nu_{\text{C=C}}$), 1250 (m, $\beta_{\text{C-H}}$), 1158 (w, $\beta_{\text{C-H}}$), 1065 (m, $\beta_{\text{C-H}}$), 1005 (s, $\beta_{\text{C-H}}$), 893 (w, $\gamma_{\text{C-H}}$), 831 (s, $\gamma_{\text{C-H}}$), 793 (s, $\gamma_{\text{C-H}}$), 730 (m, $\gamma_{\text{C-H}}$), 657 (m), 639 (m), 585 (w, $\nu_{\text{C-I}}$).

[Co(L⁷)₂]Cl₂ (7). A solution of CoCl₂·6H₂O (0.09 g, 0.39 mmol) in ethanol (10 mL) was added dropwise to a solution of L⁷ (0.10 g, 0.26 mmol) dissolved in dichloromethane (10 mL) in a 50 mL flask and stirred for 8 h at ambient temperature. A brown solid (0.066 g, 66% yield based on L⁷) was obtained upon filtration of the solution and washed with dichloromethane and dried in a desiccator. Anal. IR (KBr disc) (cm^{-1}): 3059 (w, $\nu_{\text{C-H}}$), 1608 (w, $\delta_{\text{C-H}}$), 1599 (s, *n*-pyridyl-H), 1545 (m, *n*-pyridyl-H), 1472 (s, $\nu_{\text{C=C}}$), 1428 (m, $\nu_{\text{C=C}}$), 1392 (m, $\nu_{\text{C=C}}$), 1250 (m, $\beta_{\text{C-H}}$), 1160 (w, $\beta_{\text{C-H}}$), 1065 (m, $\beta_{\text{C-H}}$), 1005 (s, $\beta_{\text{C-H}}$), 894 (w, $\gamma_{\text{C-H}}$), 830 (s, $\gamma_{\text{C-H}}$), 792 (s, $\gamma_{\text{C-H}}$), 730 (m, $\gamma_{\text{C-H}}$), 700 (w), 657 (m), 638 (m).

[Co(L⁸)₂]Cl₂ (8). A solution of CoCl₂·6H₂O (0.10 g, 0.44 mmol) in ethanol (10 mL) was added dropwise to a solution of L⁸ (0.10 g, 0.29 mmol) dissolved in dichloromethane (10 mL) in a 50 mL flask and stirred for 8 h at ambient temperature. A brown solid (0.072 g, 72% yield based on L⁸) was obtained upon filtration of the solution and washed with dichloromethane and dried in a desiccator. Anal. Calcd for C₄₂H₂₈Cl₂N₆CoCl₂·2.8CH₂Cl₂·2.6H₂O: C, 48.82; H, 3.54; N, 7.62%.

Found: C, 48.44; H, 3.05; N, 8.17 %. IR (KBr disc) (cm^{-1}): 3059 (w, $\nu_{\text{C-H}}$), 1600 (s, *n*-pyridyl-H), 1547 (m, *n*-pyridyl-H), 1473 (s, $\nu_{\text{C=C}}$), 1430 (m, $\nu_{\text{C=C}}$), 1396 (m, $\nu_{\text{C=C}}$), 1249 (m, $\beta_{\text{C-H}}$), 1158 (w, $\beta_{\text{C-H}}$), 1092 (m, $\beta_{\text{C-H}}$), 1011 (s, $\beta_{\text{C-H}}$), 897 (w, $\gamma_{\text{C-H}}$), 835 (s, $\gamma_{\text{C-H}}$), 793 (s, $\gamma_{\text{C-H}}$), 730 (m, $\nu_{\text{C-Cl}}$), 657 (m), 639 (m).

[Co(L⁹)₂]Cl₂ (9). A solution of CoCl₂·6H₂O (0.1 g, 0.46 mmol) in ethanol (10 mL) was added dropwise to a solution of L⁹ (0.10 g, 0.31 mmol) dissolved in dichloromethane (10 mL) in a 50 mL flask and stirred for 8 h at ambient temperature. A brown solid (0.070 g, 70% yield based on L⁹) was obtained upon filtration of the solution and washed with dichloromethane and dried in a desiccator. Anal. Calcd for C₄₂H₂₈F₂N₆CoCl₂·2.1CH₂Cl₂·2.4H₂O: C, 52.64; H, 3.71; N, 8.35%. Found: C, 52.46; H, 3.45; N, 8.78%. IR (KBr disc) (cm^{-1}): 3069 (w, $\nu_{\text{C-H}}$), 1599 (s, *n*-pyridyl-H), 1548 (m, *n*-pyridyl-H), 1518 (m, $\nu_{\text{C=C}}$), 1473 (s, $\nu_{\text{C=C}}$), 1433 (m, $\nu_{\text{C=C}}$), 1400 (m, $\nu_{\text{C=C}}$), 1231 (s, $\nu_{\text{C-F}}$), 1167 (s, $\beta_{\text{C-H}}$), 1013 (m, $\beta_{\text{C-H}}$), 897 (w, $\gamma_{\text{C-H}}$), 841 (s, $\gamma_{\text{C-H}}$), 793 (s, $\gamma_{\text{C-H}}$), 730 (m, $\gamma_{\text{C-H}}$), 657 (m), 639 (m) and 572 (m).