## Supporting Information

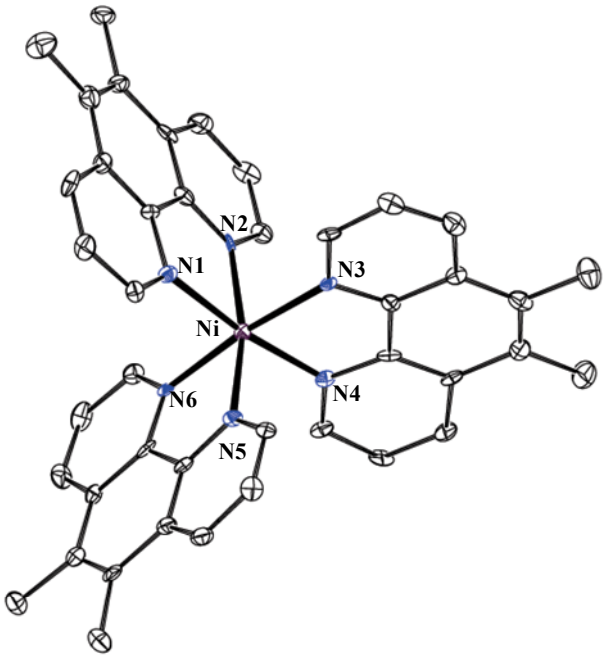



**Figure S1** ORTEP representation of the X-ray crystal structure of $NiN_6$ chromophore, with all non-hydrogen atoms shown as 50% thermal ellipsoids.

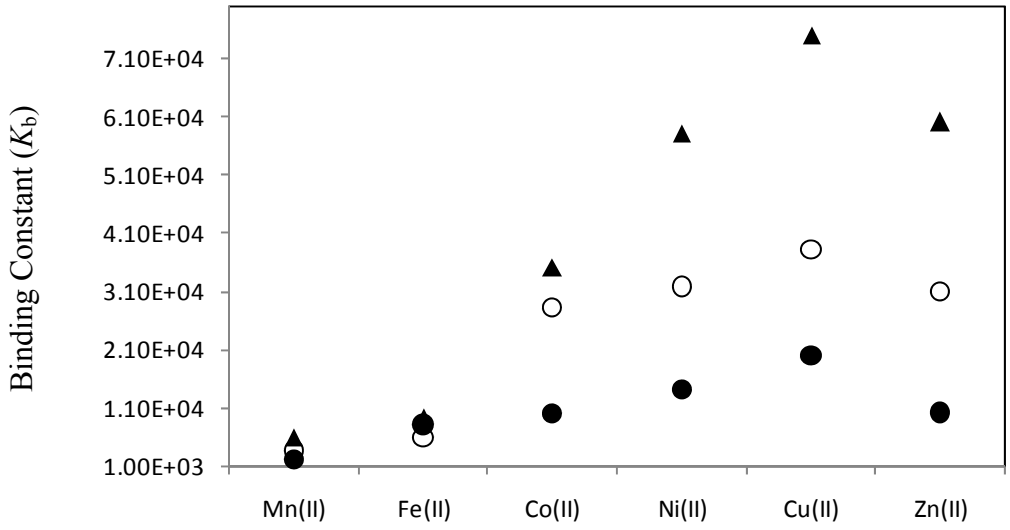



**Figure S2** DNA binding constants of Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of phen (●), 5,6-dmp (○) and dpq (▲) *vs* d electron population.

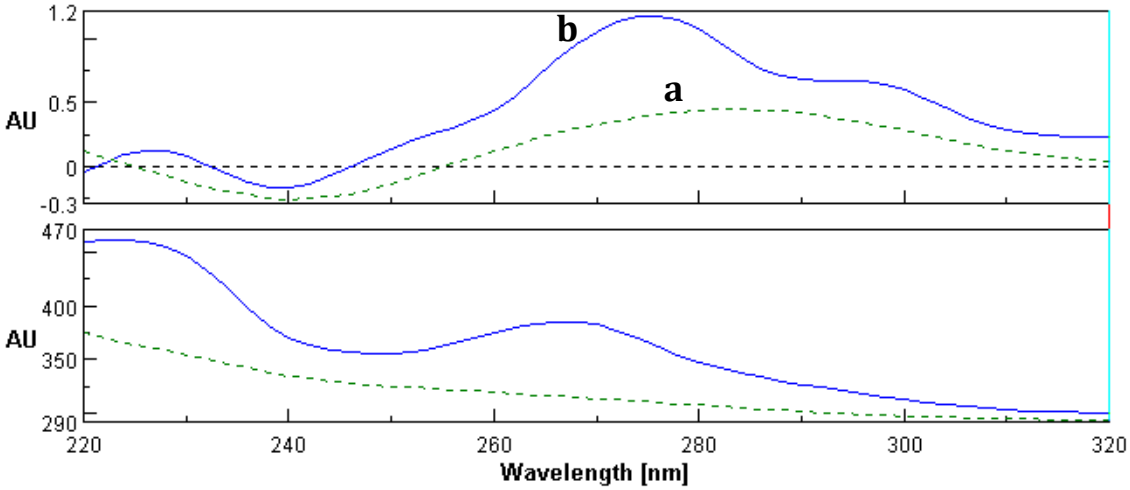



**Figure S3** Circular Dichroic spectra of CT DNA in the absence (a) and presence of (b) $[Co(phen)_3]^{2+}$ (1/R = 2); Conc of CT DNA = $2 \times 10^{-5}$ mol.dm$^3$.

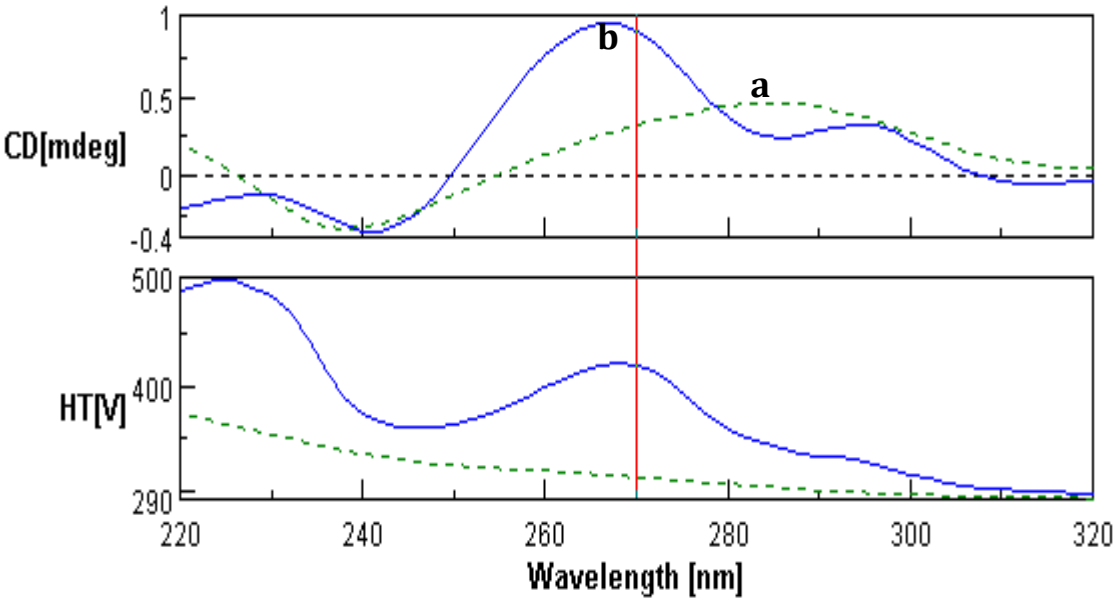



**Figure S4** Circular Dichroic spectra of CT DNA in the absence (a) and presence of (b) $[Ni(phen)_3]^{2+}$ (1/R = 2); Conc of CT DNA = $2 \times 10^{-5}$ mol.dm$^3$.

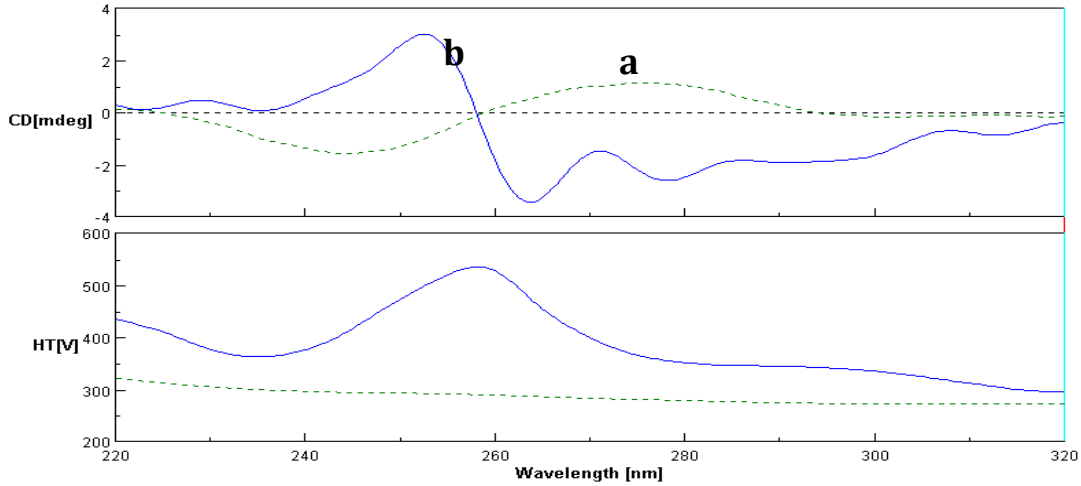



**Figure S5** Circular Dichroic spectra of CT DNA in the absence (a) and presence of (b) $[Co(dpq)_3]^{2+}$ (1/R = 2); Conc of CT DNA = $2 \times 10^{-5}$ mol.dm$^3$.

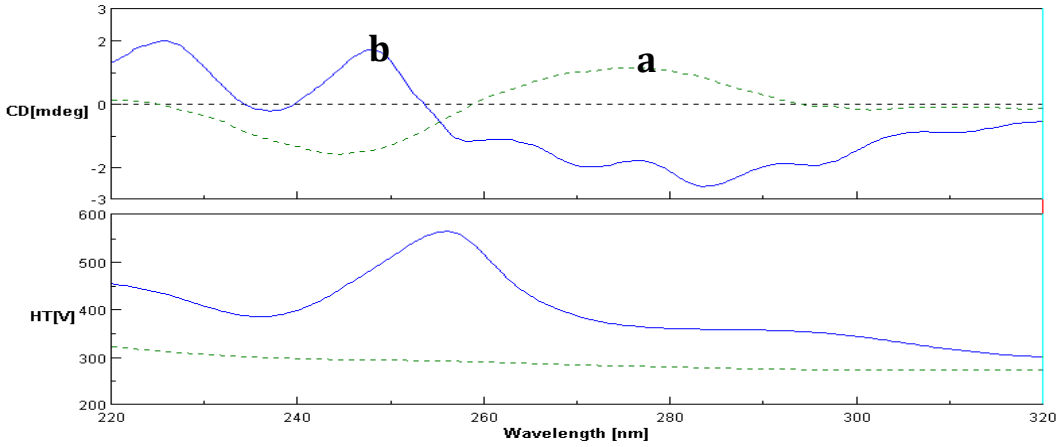



**Figure S6** Circular Dichroic spectra of CT DNA in the absence (a) and presence of (b) $[Ni(dpq)_3]^{2+}$ (1/R = 2); Conc of CT DNA = $2 \times 10^{-5}$ mol.dm$^3$.

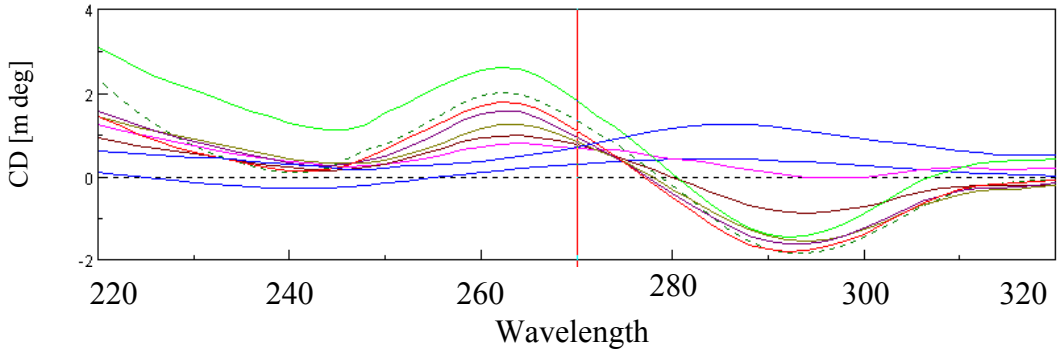



**Figure S7**. Circular Dichroism spectra of CT DNA in the absence (1/R = 0) and in presence of (1/R = 0 – 4) $[Co(5,6\text{-dmp})_3]^{2+}$. Conc of the CT DNA = $2 \times 10^{-5}$ mol.dm$^3$; Cell length = 0.2 cm.

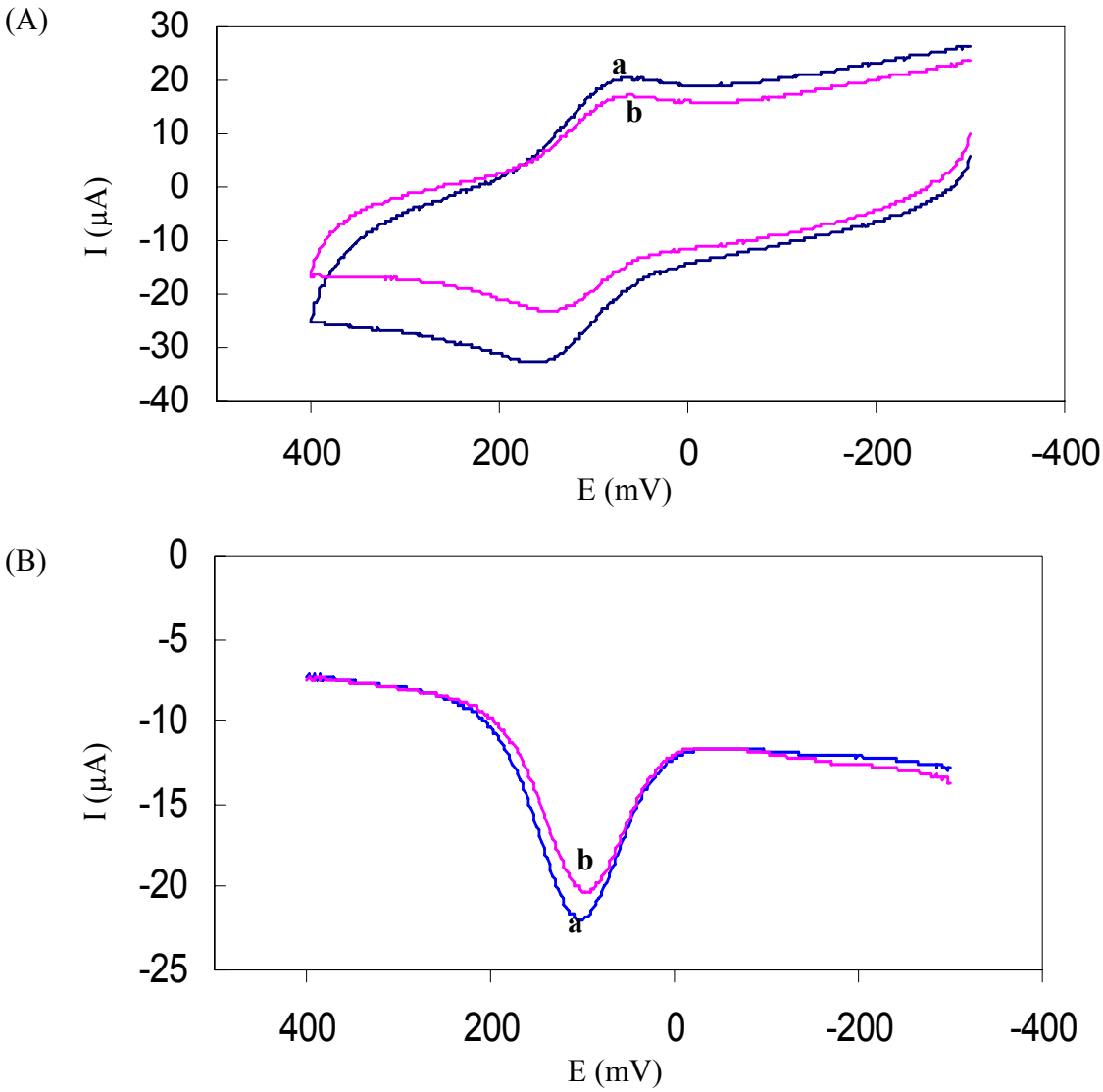
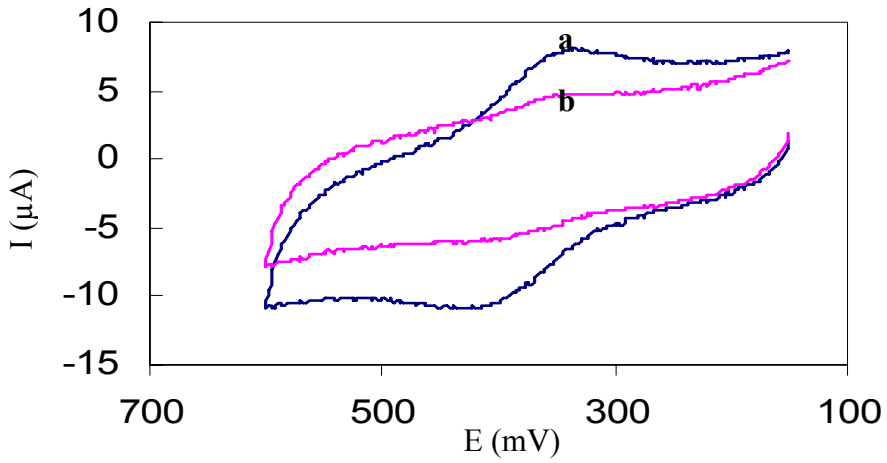



**Figure S8** (A) Cyclic Voltammograms of the complex **2** (0.5 mM) in the absence (a) and in the presence of (b) of CT DNA (R = 3) at 25.0 ± 0.2 °C at 50 mV $s^{-1}$ scan rate in 2% DMF/5 mM Tris-HCl/50 mM NaCl at pH 7.1 (B) Differential Pulse Voltammograms of the complex **2** (0.5 mM) in the absence (a) and in the presence of (b) of CT DNA (R = 3) at 25.0 ± 0.2 °C at 5 mV $s^{-1}$ scan rate in 2% DMF/5 mM Tris-HCl/50 mM NaCl at pH 7.1.

(A)




(B)

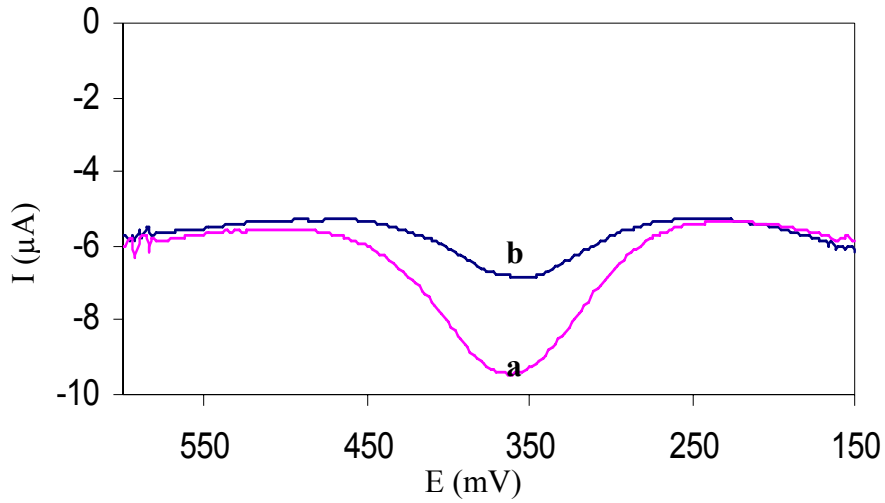



**Figure S9** (A) Cyclic Voltammograms of the complex **3** (0.5 mM) in the absence (a) and in the presence of (b) of CT DNA (R = 3) at 25.0 ± 0.2 °C at 50 mV $s^{-1}$ scan rate in 2% DMF/5 mM Tris-HCl/50 mM NaCl at pH 7.1 (B) Differential Pulse Voltammograms of the complex **3** (0.5 mM) in the absence (a) and in the presence of (b) of CT DNA (R = 3) at 25.0 ± 0.2 °C at 5 mV $s^{-1}$ scan rate in 2% DMF/5 mM Tris-HCl/50 mM NaCl at pH 7.1.

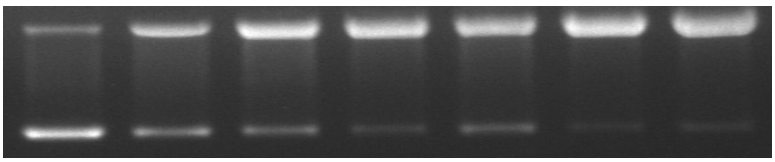



**Figure S10** Time-dependent DNA (40 μM in base pairs) cleavage by the complex **2** (0 – 60 min) in 2% DMF/5 mM Tris-HCl/50 mM NaCl at pH = 7.1 and 37 °C in the presence of $H_2O_2$ (200 μM) at 37 °C. lane 1, DNA + $H_2O_2$ + **2** (0 min); lane 2, DNA + $H_2O_2$ + **2** (10 min) ; lane 3, DNA + $H_2O_2$ + **3** (20 min); lane 4, DNA + $H_2O_2$ + **2** (30 min); lane 5, DNA + $H_2O_2$ + **2** (40 min); lane 6, DNA + $H_2O_2$ + **2** (50 min); lane 7, DNA + $H_2O_2$ + **2** (60 min). Forms I and II are supercoiled and nicked circular forms of DNA respectively.

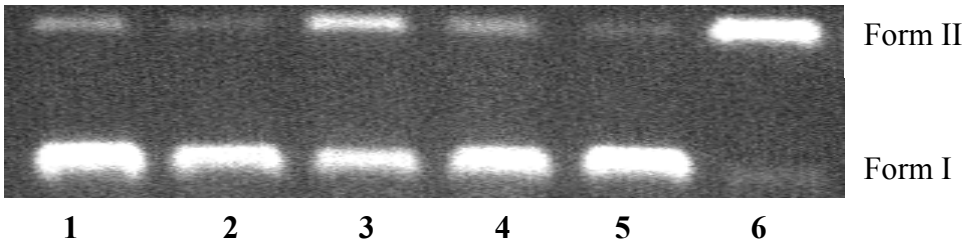
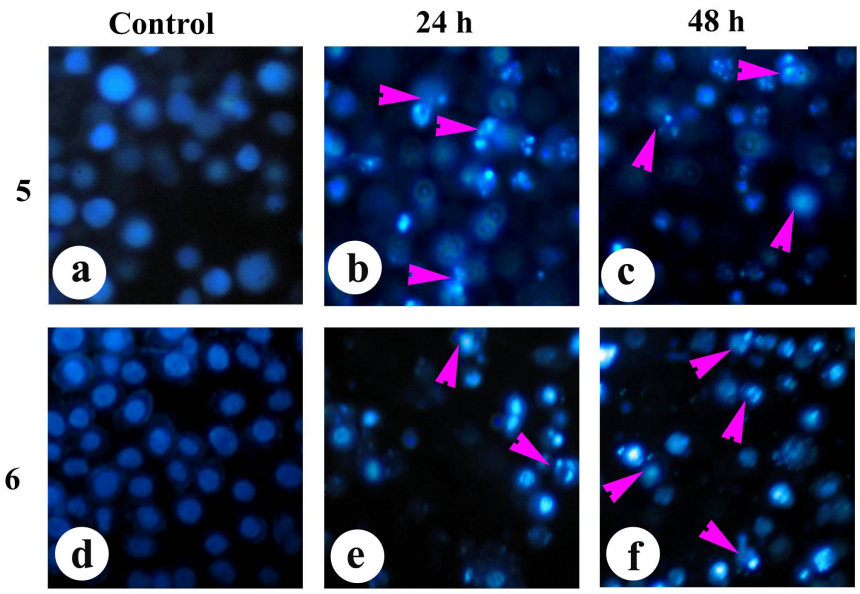



**Figure S11** Cleavage of supercoiled pUC19 DNA (40 μM in base pairs) by 10 μM complexes (**1** – **3**) in 2% DMF/5 mM Tris-HCl/50 mM NaCl at pH = 7.1 and 37 °C in the presence of $H_2O_2$ (200 μM) at 37 °C. lane 1, DNA + $H_2O_2$ + DMSO; lane 2, DNA + $H_2O_2$ + DMSO (2 μL) + **1**; lane 3, DNA + $H_2O_2$ + DMSO (2 μL ) + **3**; lane 4, DNA + $H_2O_2$ + DMSO (2 μL) + **2**; lane 5, DNA + $H_2O_2$ + Distamycin (4 μL) + **1**, lane 6, DNA + $H_2O_2$ + Distamycin (4 μL) + **2** . Forms I and II are supercoiled and nicked circular forms of DNA respectively.

(A)




(B)

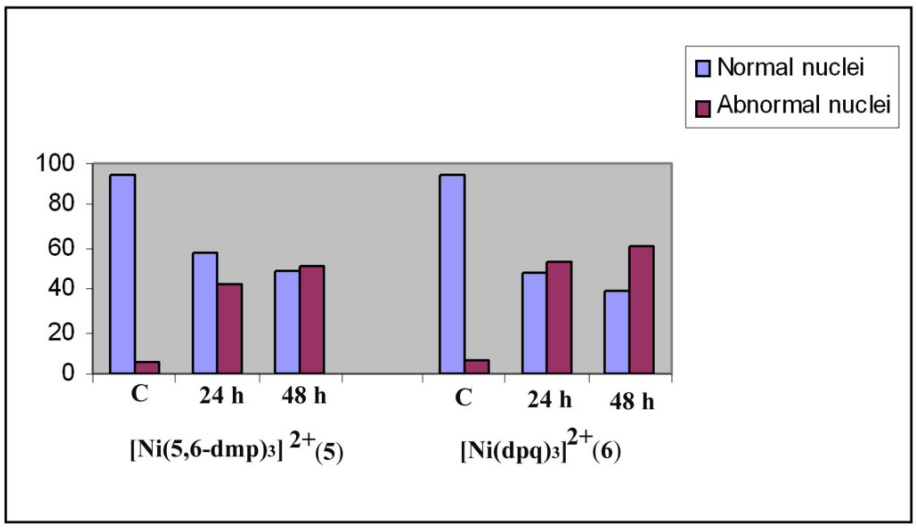



**Figure S12**. (A) Hoechst 33258 fluorescent staining of MCF-7 human breast cancer cells. (a,d) untreated cells, (b,c) treatment of complex **5**, and (e,f) complex **6** with MCF-7 cells at 24 and 48 h of incubation respectively (Arrow heads indicatie apoptotic cellular morphology include blebbing, cell shrinkage, loss if cell membrane asymmetry). (B) Graph shows manual count of apoptotic cells in percentage. (Data are mean % ± SD % of triplicate each).

**Table S1** Selected inter atomic distances and bond angles for complexes **2** and **5**.

| | **2** | | **5** |
|---|---|---|---|
| Bond Distances (Å) | | | |
| Co(1) – N(1) | 2.119(4) | Ni(1) – N(1) | 2.078(5) |
| Co(1) – N(2) | 2.113(4) | Ni(1) – N(2) | 2.079(5) |
| Co(1) – N(3) | 2.117(4) | Ni(1) – N(3) | 2.072(5) |
| Co(1) – N(4) | 2.116(4) | Ni(1) – N(4) | 2.077(5) |
| Co(1) – N(5) | 2.121(4) | Ni(1) – N(5) | 2.082(5) |
| Co(1) – N(6) | 2.138(4) | Ni(1) – N(6) | 2.084(5) |
| | | | |
| Bond Angles (º) | | | |
| N(1) – Co(1) – N(2) | 78.45(14) | N(1) – Ni(1) – N(2) | 79.6(2) |
| N(1) – Co(1) – N(3) | 94.16(14) | N(1) – Ni(1) – N(3) | 91.9(2) |
| N(1) – Co(1) – N(4) | 172.08(14) | N(1) – Ni(1) – N(4) | 98.7(2) |
| N(1) – Co(1) – N(5) | 93.16(14) | N(1) – Ni(1) – N(5) | 168.5(2) |
| N(1) – Co(1) – N(6) | 91.94(14) | N(1) – Ni(1) – N(6) | 92.5(2) |
| N(2) – Co(1) – N(3) | 91.41(14) | N(2) – Ni(1) – N(3) | 93.9(2) |
| N(2) – Co(1) – N(4) | 100.74(14) | N(2) – Ni(1) – N(4) | 172.9(2) |
| N(2) – Co(1) – N(5) | 167.26(15) | N(2) – Ni(1) – N(5) | 92.8(2) |
| N(2) – Co(1) – N(6) | 92.91(14) | N(2) – Ni(1) – N(6) | 92.5(2) |
| N(3) – Co(1) – N(4) | 77.96(14) | N(3) – Ni(1) – N(4) | 79.2(2) |
| N(3) – Co(1) – N(5) | 98.82(14) | N(3) – Ni(1) – N(5) | 97.2(2) |
| N(3) – Co(1) – N(6) | 173.13(14) | N(3) – Ni(1) – N(6) | 172.8(2) |
| N(4) – Co(1) – N(5) | 88.87(14) | N(4) – Ni(1) – N(5) | 89.8(2) |
| N(4) – Co(1) – N(6) | 95.97(14) | N(4) – Ni(1) – N(6) | 94.6(2) |
| N(5) – Co(1) – N(6) | 77.65(14) | N(5) – Ni(1) – N(6) | 79.1(2) |

**Table S2** Oxidative cleavage data of SC pUC19 DNA (40 μM, in base pair) by complexes **1 – 3** in the presence of $H_2O_2$ (200 μM).

| | | Form (%) | |
|---|---|---|---|
| Serial No | Reaction conditions | SC | NC |
| 1 | DNA control | 95.6 | 4.4 |
| 2 | DNA + $H_2O_2$ | 79.3 | 20.7 |
| 3 | DNA + $H_2O_2$ + **1** (10 μM) | 4.8 | 95.2 |
| 4 | DNA + $H_2O_2$ + **2** (10 μM) | 3.1 | 96.9 |
| 5 | DNA + $H_2O_2$ + **3** (10 μM) | 32.2 | 67.8 |

**Table S3** Concentration dependent oxidative cleavage data of SC pUC19 DNA (40 μM, in base pair) by complex **1** in the presence of $H_2O_2$ (200 μM).

| | | Form (%) | |
|---|---|---|---|
| Serial No | Reaction conditions | SC | NC |
| 1 | DNA control | 94.3 | 5.7 |
| 2 | DNA + $H_2O_2$ | 82.6 | 17.4 |
| 3 | DNA + $H_2O_2$ + **1**(2 μM) | 67.9 | 32.1 |
| 4 | DNA + $H_2O_2$ + **1**(4 μM) | 43.2 | 56.8 |
| 5 | DNA + $H_2O_2$ + **1**(6 μM) | 29.8 | 70.2 |
| 6 | DNA + $H_2O_2$ + **1**(8 μM) | 18.7 | 81.3 |
| 7 | DNA + $H_2O_2$ + **1**(10 μM) | 3.8 | 96.2 |
| 8 | DNA + $H_2O_2$ + **1**(20 μM) | 1.2 | 98.8 |

**Table S4** Concentration dependent oxidative cleavage data of SC pUC19 DNA (40 μM, in base pair) by complex **2** in the presence of $H_2O_2$ (200 μM).

| Serial No | Reaction conditions | Form (%) | |
|---|---|---|---|
| | | SC | NC |
| 1 | DNA control | 94.3 | 5.7 |
| 2 | DNA + $H_2O_2$ | 82.6 | 17.4 |
| 3 | DNA + $H_2O_2$ + **2**(2 μM) | 51.6 | 48.4 |
| 4 | DNA + $H_2O_2$ + **2**(4 μM) | 23.0 | 77.0 |
| 5 | DNA + $H_2O_2$ + **2**(6 μM) | 9.0 | 91.0 |
| 6 | DNA + $H_2O_2$ + **2**(8 μM) | 7.9 | 92.1 |
| 7 | DNA + $H_2O_2$ + **2**(10 μM) | 0.9 | 99.1 |
| 8 | DNA + $H_2O_2$ + **2**(20 μM) | 0.5 | 99.5 |

**Table S5** Time dependent oxidative cleavage data of SC pUC19 DNA (40 μM, in base pairs) by complex **1** (10 μM**)** in the presence of $H_2O_2$ (200 μM).

| Serial no | Reaction conditions ` | Form% | |
|---|---|---|---|
| | | SC | NC |
| 1 | DNA + $H_2O_2$ + **1**(0 min) | 95.0 | 5.0 |
| 2 | DNA + $H_2O_2$ + **1**(10 min) | 17.7 | 82.3 |
| 3 | DNA + $H_2O_2$ + **1**(20 min) | 6.3 | 93.7 |
| 4 | DNA + $H_2O_2$ + **1**(30 min) | 5.8 | 94.2 |
| 5 | DNA + $H_2O_2$ + **1**(40 min) | 4.0 | 96.0 |
| 6 | DNA + $H_2O_2$ + **1**(50 min) | 2.9 | 97.1 |
| 7 | DNA + $H_2O_2$ + **1**(60 min) | 1.7 | 98.3 |

**Table S6** Time dependent oxidative cleavage data of SC pUC19 DNA (40 μM, in base pairs) by complex **2** (10 μM**)** in the presence of $H_2O_2$ (200 μM).

| Serial no | Reaction conditions | Form% | |
|---|---|---|---|
| | | SC | NC |
| 1 | DNA + $H_2O_2$ + **2**(0 min) | 95.0 | 5.0 |
| 2 | DNA + $H_2O_2$ + **2**(10 min) | 6.0 | 94.0 |
| 3 | DNA + $H_2O_2$ + **2**(20 min) | 5.3 | 94.7 |
| 4 | DNA + $H_2O_2$ + **2**(30 min) | 5.0 | 95.0 |
| 5 | DNA + $H_2O_2$ + **2**(40 min) | 3.7 | 96.3 |
| 6 | DNA + $H_2O_2$ + **2**(50 min) | 1.9 | 98.1 |
| 7 | DNA + $H_2O_2$ + **2**(60 min) | 1.0 | 99.0 |

**Table S7** *In vitro* Cytotoxicity Assays for complexes **1 – 6** and cisplatin against human breast cancer cell line (MCF – 7)[a].

| Complexes | | [a]$IC_{50}$ (μM) | |
|---|---|---|---|
| | | 24 h | 48 h |
| $[Co(phen)_3]^{2+}$ | (**1**) | 30.0 ± 1.0 | 28.0 ± 0.5 |
| $[Co(5,6\text{-}dmp)_3]^{2+}$ | (**2**) | 20.0 ± 0.9 | 15.0 ± 1.0 |
| $[Co(dpq_3]^{2+}$ | (**3**) | 25.0 ± 0.7 | 20.0 ± 0.7 |
| $[Ni(phen)_3]^{2+}$ | (**4**) | 10.0 ± 1.0 | 8.0 ± 0.80 |
| $[Ni(5,6\text{-}dmp)_3]^{2+}$ | (**5**) | 3.0 ± 0.02 | 2.0 ± 0.04 |
| $[Ni(dpq_3]^{2+}$ | (**6**) | 3.0 ± 0.03 | 2.0 ± 0.06 |
| Cisplatin | | 80.0 ± 1.1 | 70.0 ± 3.2 |

[a]Data are mean ± SD of three replicates each. [a]$IC_{50}$ = concentration of drug required to inhibit growth of 50% of the cancer cells (in μM).