Supplementary information

Magneto-structural correlation, antioxidant, DNA interaction and growth inhibition activities of new chloro-bridged phenolate complexes

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Table S1 Selected bond lengths (Å) and bond angles (º) for complex **4**.

Bond lengths (Å)			
C(1)–O(1)	1.302(3)	C(1)–C(2)	1.401(4)
C(1)–C(6)	1.422(3)	Ni(1)–N(1)	2.0085(18)
Ni(1)–Cl(1)	2.3880(5)	Ni(1)–O(3)	2.1181(16)
Ni(1)–N(2)	2.222(2)	Cl(1)–Ni(1)#1	2.3880(5)
Ni(1)–O(1)	1.9974(16)	Cl(2')–Cl(2')#2	1.12(2)
Ni(1)–O(2)	2.0748(17)	Ni(1)–Ni(1)#1	4.096(4)
Bond angles (º)			
C(7)–N(1)–Ni(1)	124.59(16)	N(1)–Ni(1)–O(3)	85.67(7)
C(8)–N(1)–Ni(1)	113.96(15)	O(2)–Ni(1)–O(3)	176.51(7)
C(9)–N(2)–Ni(1)	101.90(14)	O(1)–Ni(1)–N(2)	172.08(7)
C(13)–N(2)–Ni(1)	109.22(16)	N(1)–Ni(1)–N(2)	82.46(8)
C(10)–N(2)–Ni(1)	111.60(16)	O(2)–Ni(1)–N(2)	89.72(7)
C(10')–N(2)–Ni(1)	130.9(9)	O(3)–Ni(1)–N(2)	88.55(7)
C(13')–N(2)–Ni(1)	126.6(7)	O(1)–Ni(1)–Cl(1)	89.35(5)
C(1)–O(1)–Ni(1)	126.29(14)	N(1)–Ni(1)–Cl(1)	172.80(6)
C(14)–O(2)–Ni(1)	122.14(16)	O(2)–Ni(1)–Cl(1)	90.04(5)
Ni(1)–O(2)–H(2A)	114(2)	O(3)–Ni(1)–Cl(1)	87.22(5)
C(15)–O(3)–Ni(1)	124.21(16)	N(2)–Ni(1)–Cl(1)	98.47(5)
Ni(1)–O(3)–H(3A)	117.7	Ni(1)–Cl(1)–Ni(1)#1	118.10(4)
O(1)–Ni(1)–N(1)	89.93(7)	Cl(2')#2–Cl(2')–N(3')	156.8(14)
O(1)–Ni(1)–O(2)	89.04(7)	N(1)–Ni(1)–O(3)	85.67(7)
N(1)–Ni(1)–O(2)	97.11(7)	O(2)–Ni(1)–O(3)	176.51(7)
O(1)–Ni(1)–O(3)	93.09(7)		

Symmetry transformations used to generate equivalent atoms:
#1: –x + 1, y, –z + 3/2; #2: –x + 2, y, –z + 3/2

Table S2 Hydrogen bonding parameters [Å and º] for complex **4**.

D–H…A	d(D–H)	d(H…A)	d(D…A)	*L*(DHA)
N(3)–H(3B)...Cl(2)	0.90	2.22	3.104(3)	168.8
N(3)–H(3C)...Cl(3)#3	0.90	2.22	3.068(4)	156.3
O(3)–H(3A)...O(4)	0.82	1.92	2.732(3)	170.2
O(2)–H(2A)...O(1)#1	0.896(10)	1.741(10)	2.635(2)	176(3)
O(4)–H(4A)...Cl(3)	0.917(10)	2.240(11)	3.155(3)	176(3)
O(4)–H(4B)...Cl(3)#4	0.910(10)	2.320(16)	3.196(3)	161(3)

Symmetry transformations used to generate equivalent atoms:

#1: –x + 1, y, –z + 3/2; #2: –x + 2, y, –z + 3/2; #3: x + 1, y, z; #4: –x, –y + 1, –z + 1

Table S3 Selected bond lengths (Å) and bond angles (º) for complex **8**.

Bond lengths (Å)			
C(4)–O(1)	1.315(5)	C(17)–O(2)	1.310(5)
C(3)–C(4)	1.411(6)	C(16)–C(17)	1.411(6)
Cu(1)–N(1)	1.955(3)	Cu(2)–N(4)	1.964(3)
Cu(1)–N(2)	2.104(3)	Cu(2)–N(5)	2.089(3)
Cu(1)–O(1)	1.945(3)	Cu(2)–O(2)	1.935(3)
Cu(1)–Cl(1)	2.2702(12)	Cu(2)–Cl(3)	2.3246(12)
Cu(1)–Cl(2)	2.6261(12)	Cu(2)–Cl(2)	2.5242(12)
Cu(1)–Cu(2)	4.612(8)		
Bond angles (º)			
C(7)–N(1)–Cu(1)	124.5(3)	C(20)–N(4)–Cu(2)	126.2(3)
C(8)–N(1)–Cu(1)	113.5(3)	C(21)–N(4)–Cu(2)	114.2(3)
C(9)–N(2)–Cu(1)	104.4(2)	C(22)–N(5)–Cu(2)	102.7(2)
C(10)–N(2)–Cu(1)	107.6(2)	C(23)–N(5)–Cu(2)	113.8(2)
C(13)–N(2)–Cu(1)	113.1(3)	C(26)–N(5)–Cu(2)	109.1(2)
C(4)–O(1)–Cu(1)	123.6(2)	C(17)–O(2)–Cu(2)	127.4(3)
O(1)–Cu(1)–N(1)	90.37(13)	O(2)–Cu(2)–N(4)	92.14(13)
O(1)–Cu(1)–N(2)	167.64(13)	O(2)–Cu(2)–N(5)	173.97(13)
N(1)–Cu(1)–N(2)	84.20(13)	N(4)–Cu(2)–N(5)	83.53(13)
O(1)–Cu(1)–Cl(1)	88.38(8)	O(2)–Cu(2)–Cl(3)	89.37(10)
N(1)–Cu(1)–Cl(1)	167.48(11)	N(4)–Cu(2)–Cl(3)	154.82(12)
N(2)–Cu(1)–Cl(1)	94.50(10)	N(5)–Cu(2)–Cl(3)	92.78(9)
O(1)–Cu(1)–Cl(2)	98.46(9)	O(2)–Cu(2)–Cl(2)	91.67(11)
N(1)–Cu(1)–Cl(2)	87.80(10)	N(4)–Cu(2)–Cl(2)	100.91(11)
N(2)–Cu(1)–Cl(2)	92.44(10)	N(5)–Cu(2)–Cl(2)	93.27(10)
Cl(1)–Cu(1)–Cl(2)	104.71(5)	Cl(3)–Cu(2)–Cl(2)	104.18(4)
Cu(2)–Cl(2)–Cu(1)	127.11(4)		

Table S4 Hydrogen bonding parameters [Å and º] for complex **8**.

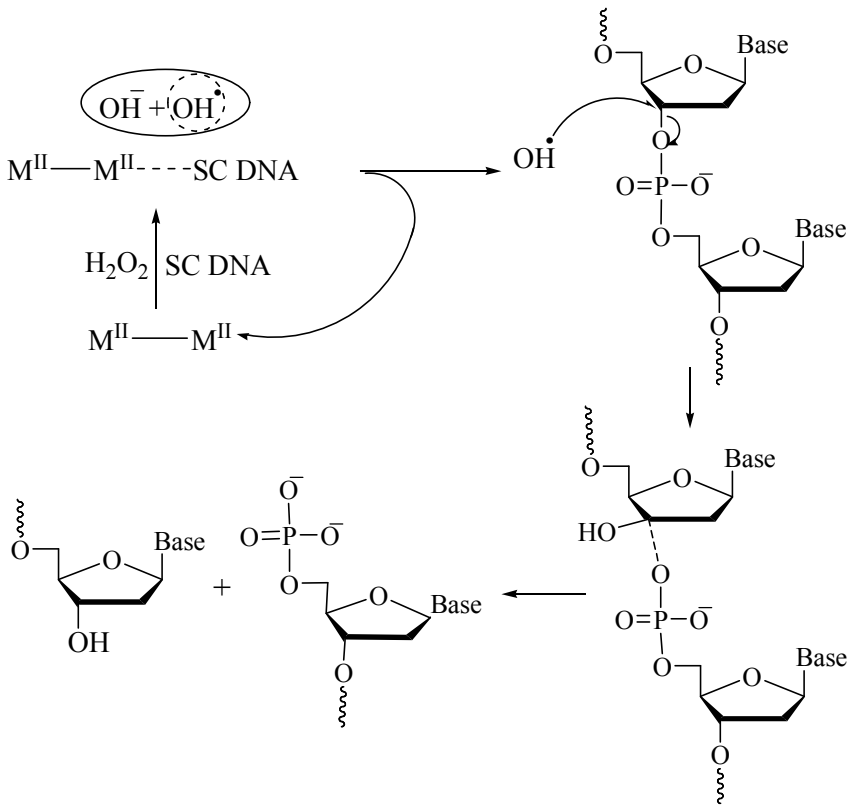
D–H…A	d(D–H)	d(H…A)	d(D…A)	*L*(DHA)
C(7)–H(7)...O(8)#1	0.93	2.64	3.556(6)	167.7
C(10)–H(10B)...Cl(1)	0.97	2.85	3.462(4)	122.1
C(11)–H(11A)...O(9)#2	0.97	2.61	3.341(8)	132.0
C(11)–H(11B)...Cl(1)#2	0.97	2.73	3.513(5)	137.6
C(12)–H(12A)...Cl(4)#2	0.97	2.91	3.570(5)	126.4
C(12)–H(12B)...Br(1)#3	0.97	3.02	3.805(4)	138.7
C(13)–H(13A)...Cl(1)	0.97	2.77	3.390(4)	122.2
C(13)–H(13B)...Cl(2)	0.97	2.83	3.485(4)	126.0
C(22)–H(22B)...Cl(3)#4	0.97	2.90	3.864(4)	171.8
C(23)–H(23A)...Cl(2)	0.97	2.77	3.405(4)	124.0
C(23)–H(23B)...Cl(3)	0.97	2.80	3.413(4)	122.0
C(24)–H(24B)...Cl(3)#4	0.97	2.78	3.553(4)	137.7
C(25)–H(25A)...Cl(3)#4	0.97	2.79	3.563(4)	136.8
C(25)–H(25A)...Br(2)#5	0.97	2.99	3.499(4)	114.3
C(25)–H(25B)...Cl(2)#4	0.97	2.88	3.361(4)	111.6
C(26)–H(26A)...Cl(3)	0.97	2.80	3.410(4)	121.5
N(3)–H(3A)...O(1)#2	0.90	1.86	2.757(4)	176.7
N(3)–H(3B)...O(8)	0.90	1.91	2.808(5)	172.0
N(6)–H(6A)...O(2)#4	0.90	2.00	2.861(4)	160.0
N(6)–H(6B)...Cl(4)#6	0.90	2.14	3.038(4)	172.1
O(8)–H(8C)...O(7)	0.908(19)	2.04(4)	2.823(6)	143(5)
O(8)–H(8D)...O(3)#7	0.942(19)	1.95(3)	2.860(6)	163(6)
O(9)–H(9C)...O(5)#5	0.985(19)	1.82(2)	2.786(8)	165(6)
O(9)–H(9D)...Cl(4)#8	0.942(19)	2.15(2)	3.094(6)	175(5)

Symmetry transformations used to generate equivalent atoms:
#1: x + 1/2, –y + 1/2, z + 1/2; #2: –x + 1/2, y + 1/2, –z + 1/2; #3: x–1/2, –y + 1/2, z – 1/2;
#4: –x + 3/2, y – 1/2, –z + 1/2; #5: –x + 1, –y, –z; #6: x + 1, y, z;
#7: x – 1, y, z; #8: –x + 1/2, y – 1/2, –z + 1/2

Table S5 Electrochemical data for the nickel(II) and copper(II) complexes (**1**–**8**).

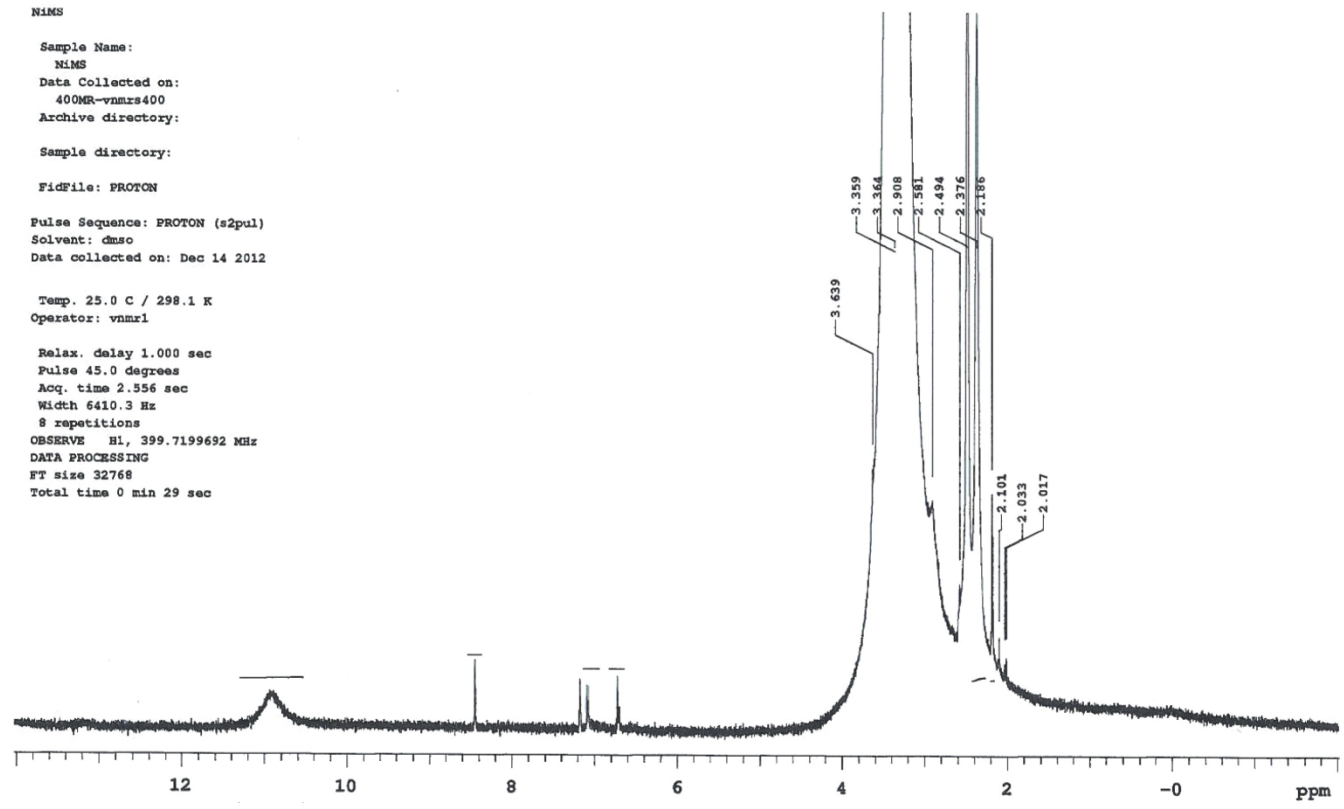
Complexes	Reduction		Oxidation							
	E^1_{pc}	E^2_{pc}	E^1_{pc}	E^1_{pa}	$E^1_{1/2}$	ΔE^1_p	E^2_{pc}	E^2_{pa}	$E^2_{1/2}$	ΔE^2_p
1	–0.70	–1.49	0.95	0.76	0.86	190	1.60	1.36	1.48	240
2	–0.77	–1.52	0.91	0.73	0.82	180	1.55	1.33	1.44	220
3	–0.68	–1.51	0.97	0.71	0.84	260	1.70	1.41	1.40	290
4	–0.69	–1.39	0.96	0.75	0.85	210	1.58	1.25	1.41	330
5	–0.82	–1.43	-	-	-	-	-	-	-	-
6	–0.85	–1.66	-	-	-	-	-	-	-	-
7	–0.79	–1.42	-	-	-	-	-	-	-	-
8	–0.81	–1.34	-	-	-	-	-	-	-	-

CV measured at 100 mVs^{-1}. *E* (V) *vs*. Ag/AgCl conditions: GC working, Pt wire counter and Ag/AgCl reference electrodes; Supporting electrolyte, TBAP (0.1 M); Complex concentration at 1 mM.



Scheme S1. A possible mechanism for oxidative cleavage of plasmid DNA.

(a)



(b)

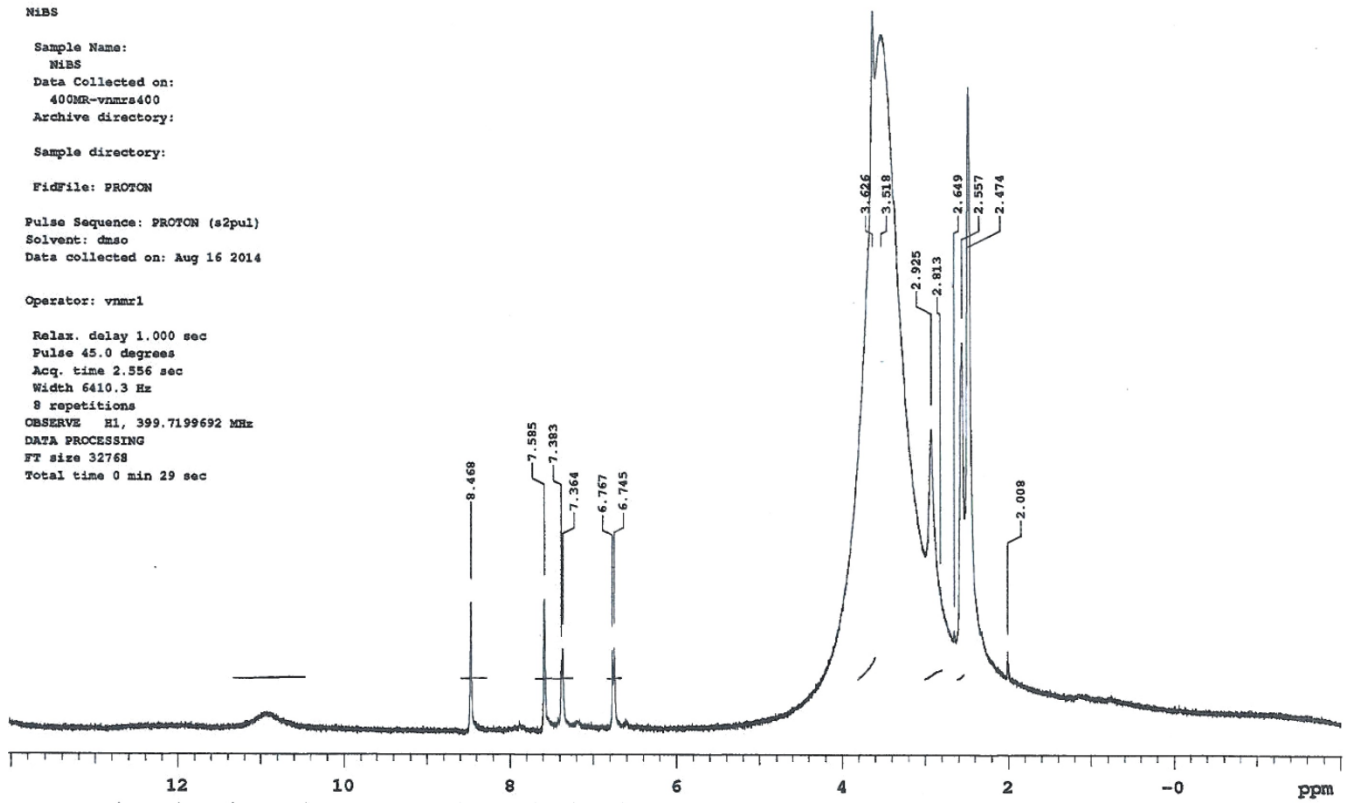


Fig. S1 ^{1}H NMR spectra of the nickel(II) complexes **2** (a) and **4** (b).

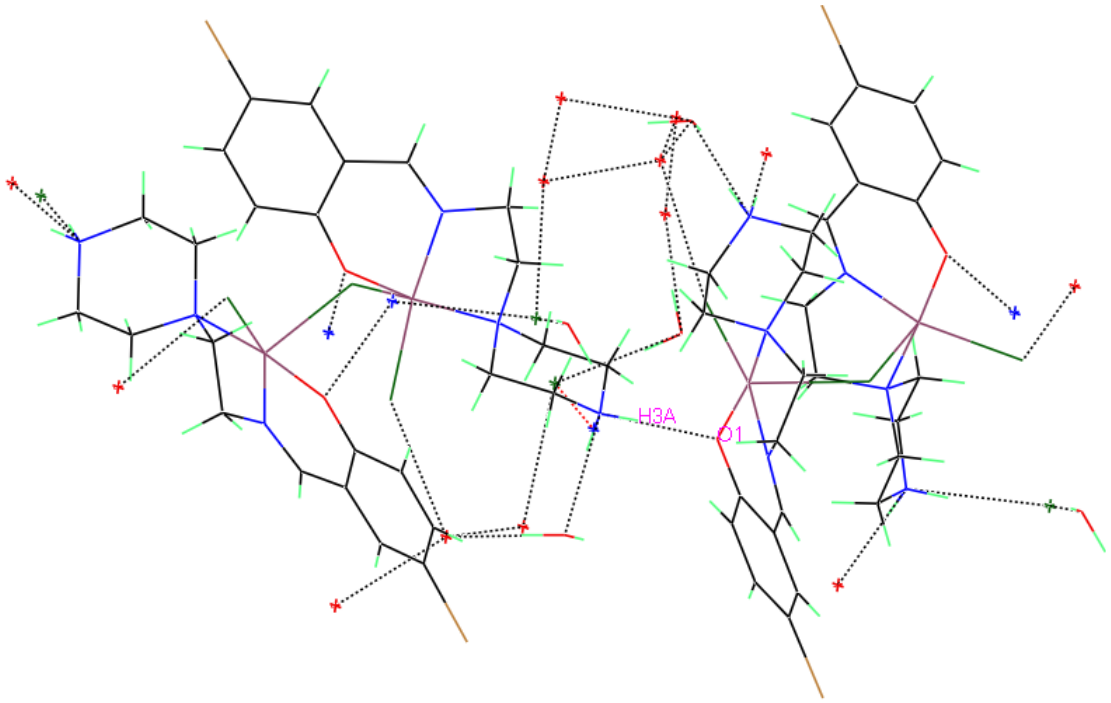


Fig. S2 Intra- and intermolecular hydrogen bonding network in complex **8**.

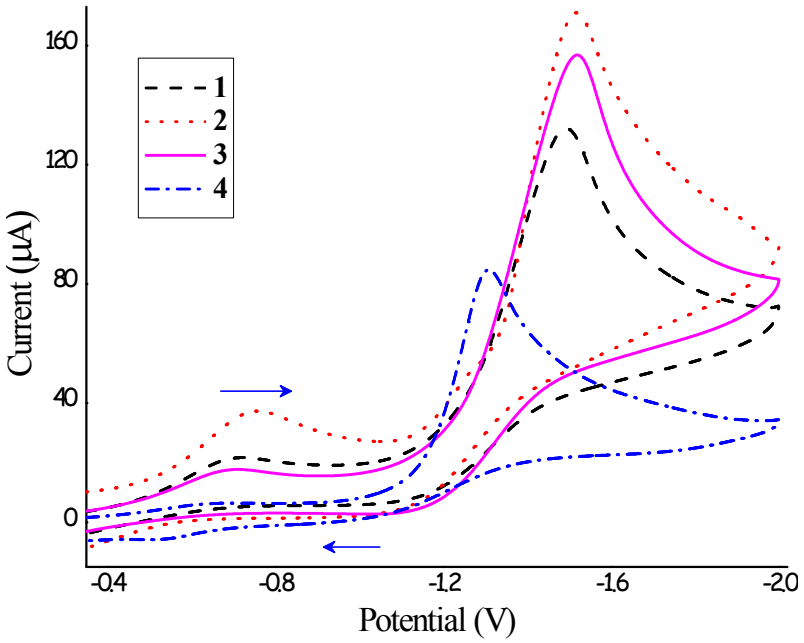


Fig. S3 Cyclic voltammograms of the dinuclear nickel(II) complexes (**1**–**4**) (reduction process).

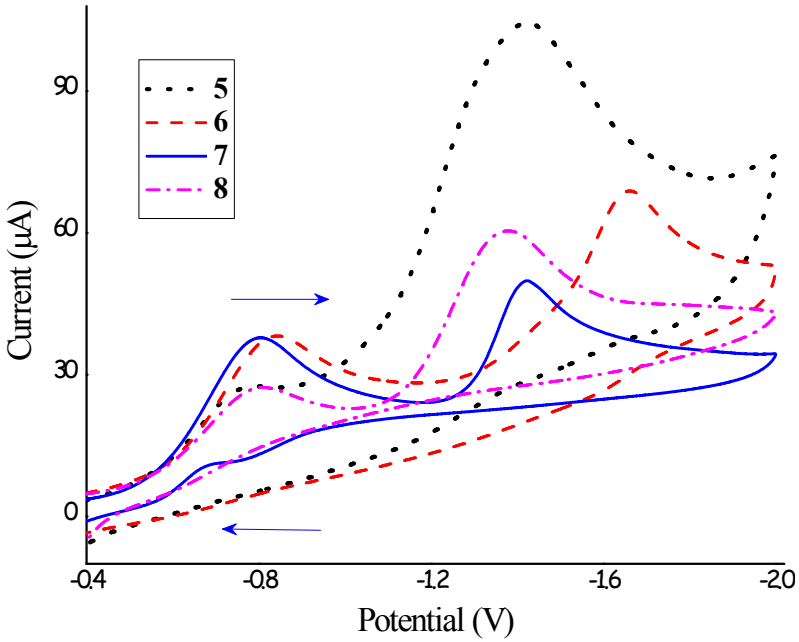


Fig. S4 Cyclic voltammograms of the dinuclear copper(II) complexes (**5**–**8**) (reduction process).

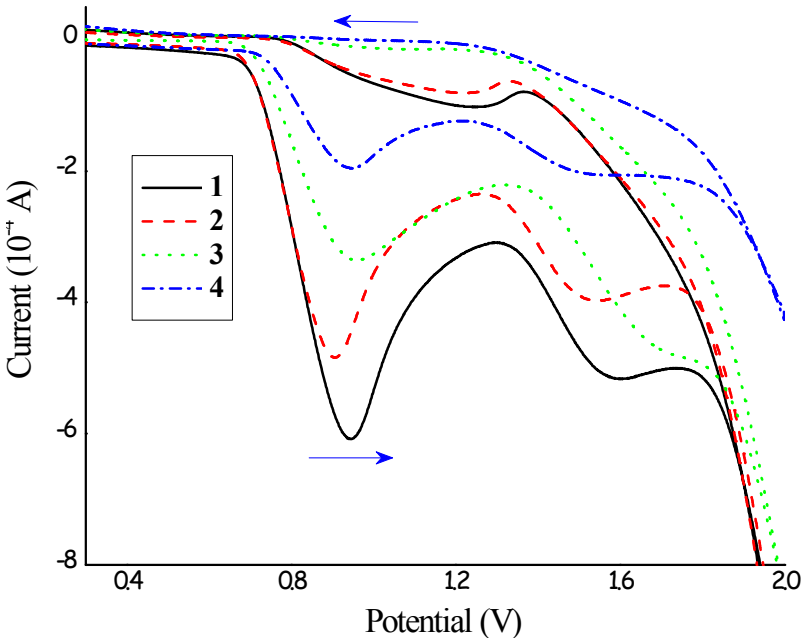


Fig. S5 Cyclic voltammograms of the dinuclear nickel(II) complexes (**1**–**4**) (oxidation process).

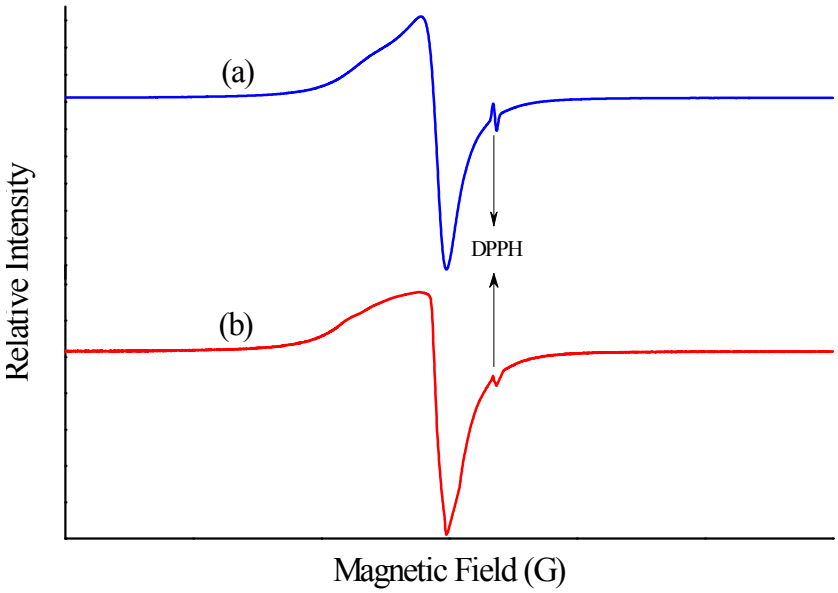


Fig. S6 X-band EPR spectra of copper(II) complexes **5** (a) and **8** (b) in DMF solution.

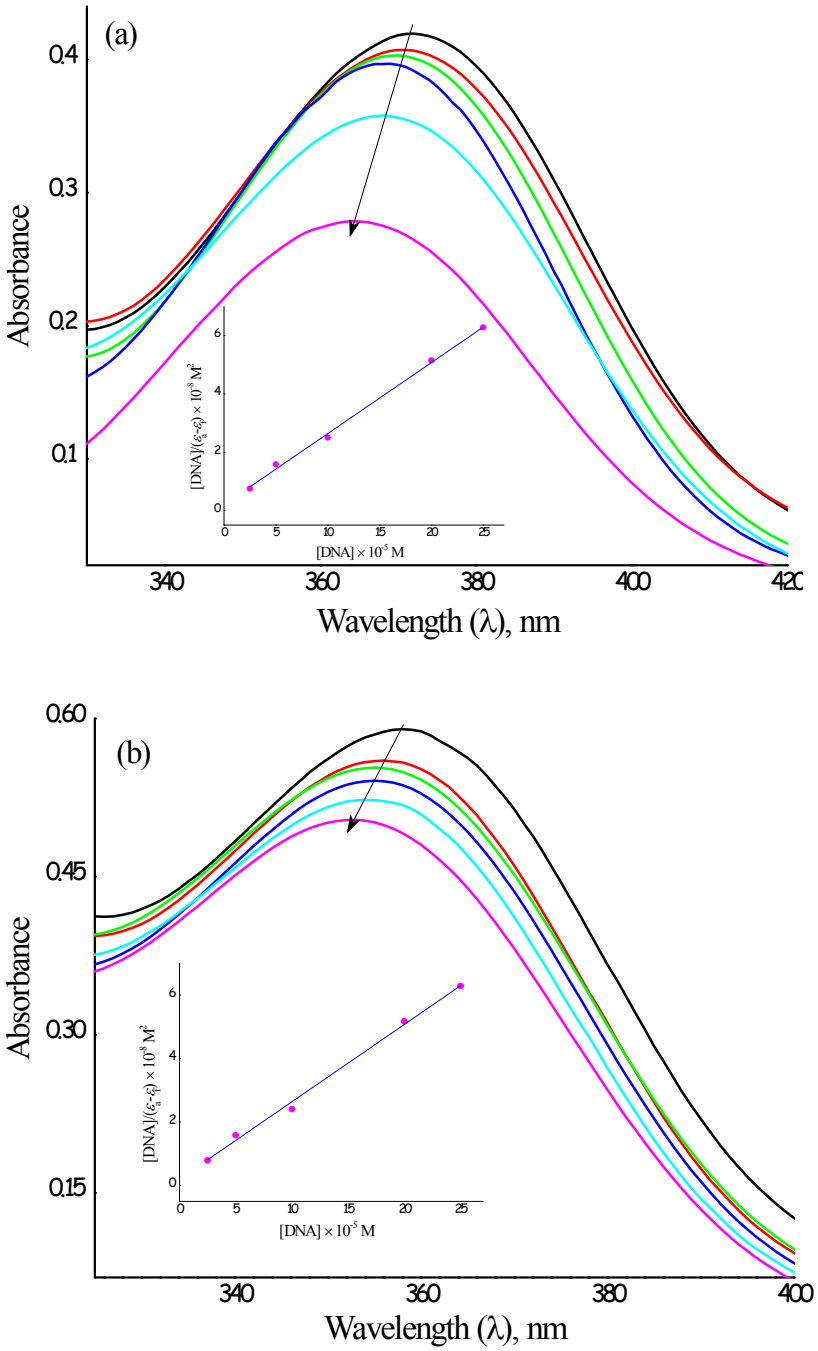


Fig. S7 Absorption spectra of complexes **1** (a) & **2** (a) (50 μM) in Tris-HCl/NaCl (pH 7.2) buffer upon addition of CT-DNA (0–500 μM). Arrow shows the absorption decreases upon increasing concentration of DNA. Inset: Plot of [DNA]/(ε_a–ε_f) *versus* [DNA] for absorption titration of CT-DNA with the complex.

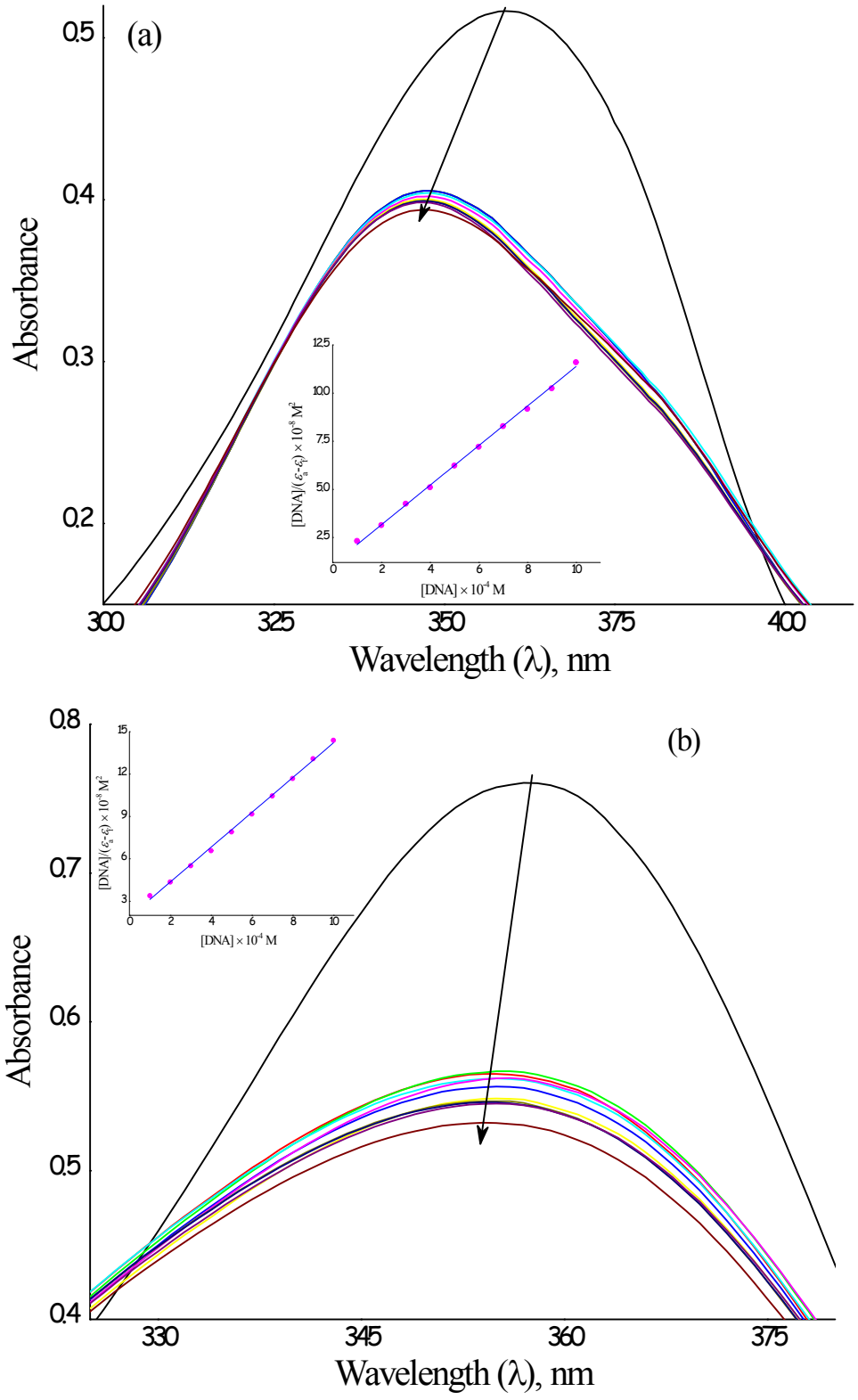


Fig. S8 Absorption spectra of complex **5** (a) & **6** (b) (50 μM) in Tris-HCl/NaCl (pH 7.2) buffer upon addition of CT-DNA (0–500 μM). Arrow shows the absorption decreases upon increasing concentration of DNA. Inset: Plot of [DNA]/(ε_a–ε_f) *versus* [DNA] for absorption titration of CT-DNA with the complex.

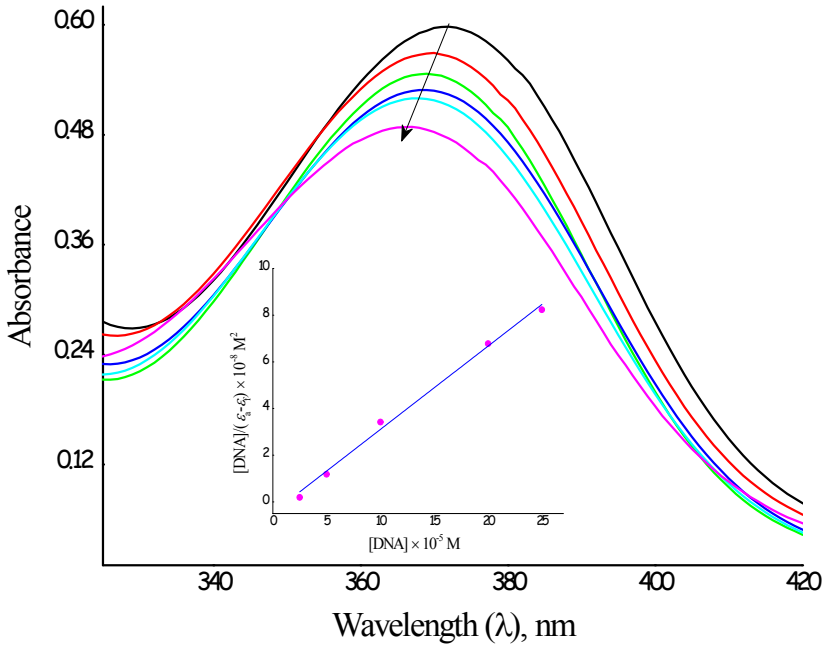


Fig. S9 Absorption spectra of complex **8** (50 μM) in Tris-HCl/NaCl (pH 7.2) buffer upon addition of CT-DNA (0–500 μM). Arrow shows the absorption decreases upon increasing concentration of DNA. Inset: Plot of [DNA]/(ε_a–ε_f) *versus* [DNA] for absorption titration of CT-DNA with the complex.

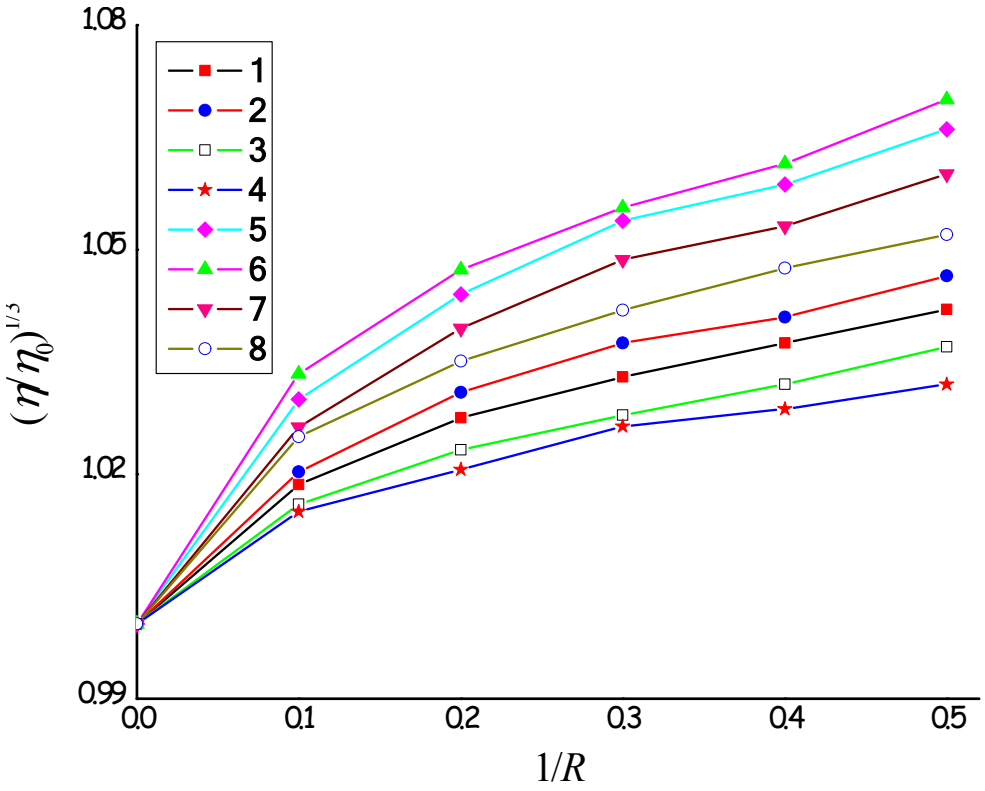


Fig. S10 Effect of complexes **1**–**8** on the viscosity of CT-DNA. Relative specific viscosity *versus* 1/*R* (*R* = [DNA]/[Complex], [DNA] = 200 μM, [Complex] = 0–100 μM).

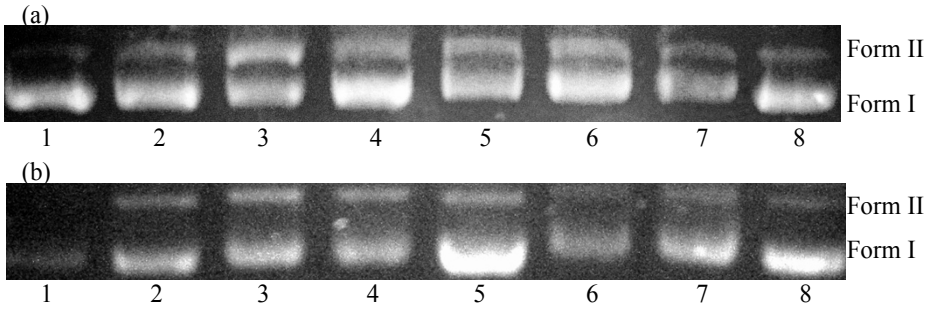


Fig. S11 Hydrolytic cleavage of pBR322 DNA (33.3 μM) by **2** (a) and **4** (b) in 50 mM Tris–HCl/NaCl buffer (pH 7.2). Lane 1, DNA alone; lane 2, DNA + **2**/**4** (25 μM); lane 3, DNA + **2**/**4** (50 μM); lane 4, DNA + **2**/**4** (75 μM); lane 5, DNA + **2**/**4** (100 μM); lane 6, DNA + **2**/**4** (150 μM); lane 7, DNA + **2**/**4** (200 μM); lane 8, DNA + **2**/**4** (250 μM).

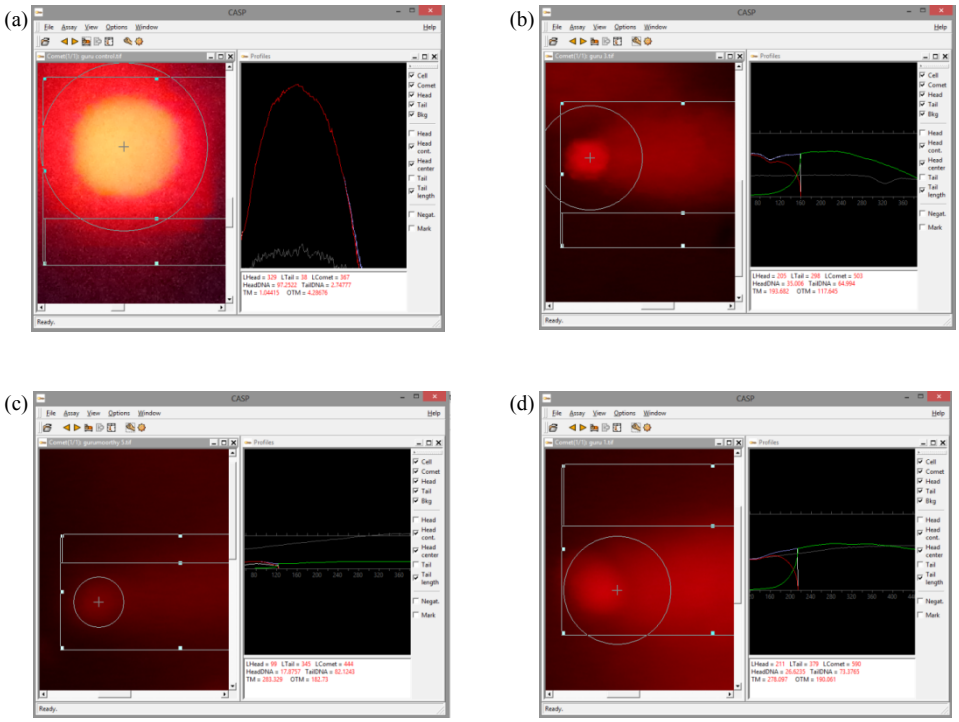


Fig. S12 The analysis of comet tail length by CASP software: Control (a) and complexes **2** (b), **6** (c) and **8** (d).