Electronic Supplementary Information for Dalton Transactions

DNA binding and oxidative DNA cleavage activity of (μ-oxo)diiron(III) complexes in visible light

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Electronic Supplementary Information

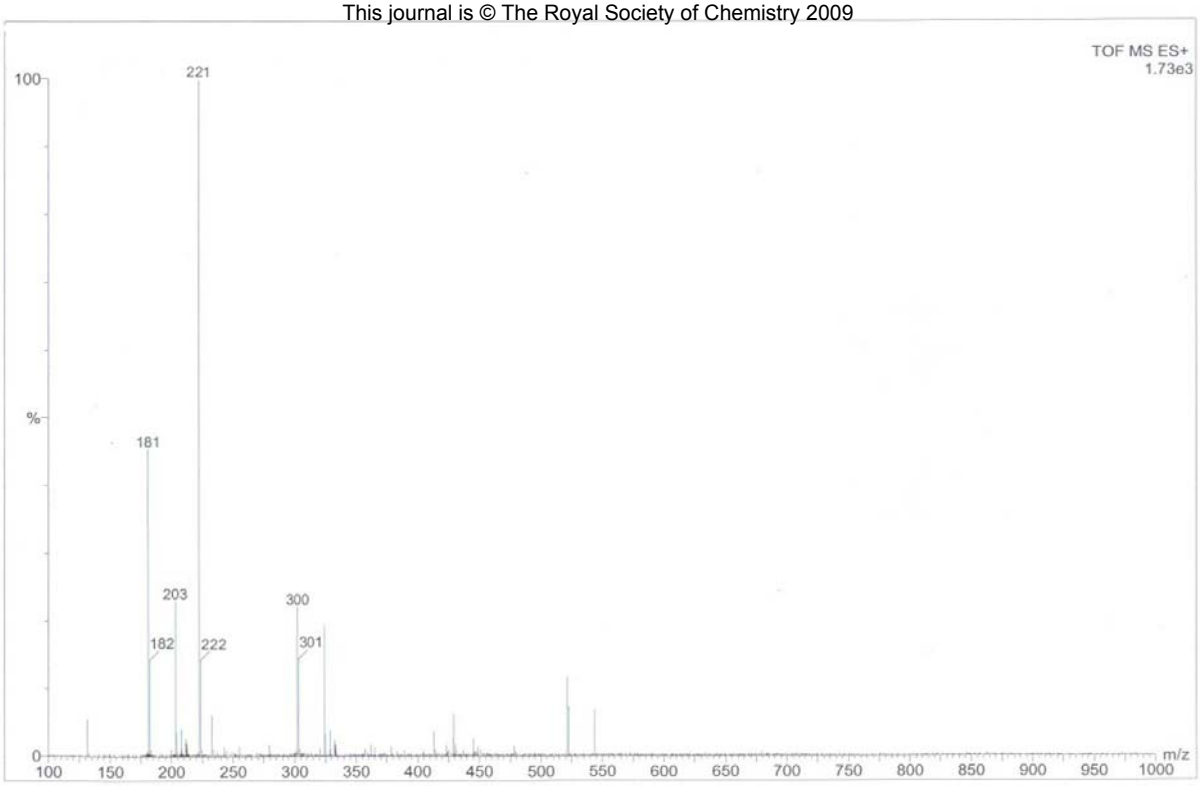


Fig. S1. ESI-MS spectrum of complex **1** in H_2O showing the parent ion peak at m/z 221 $(M-4ClO_4)^{4+}$.

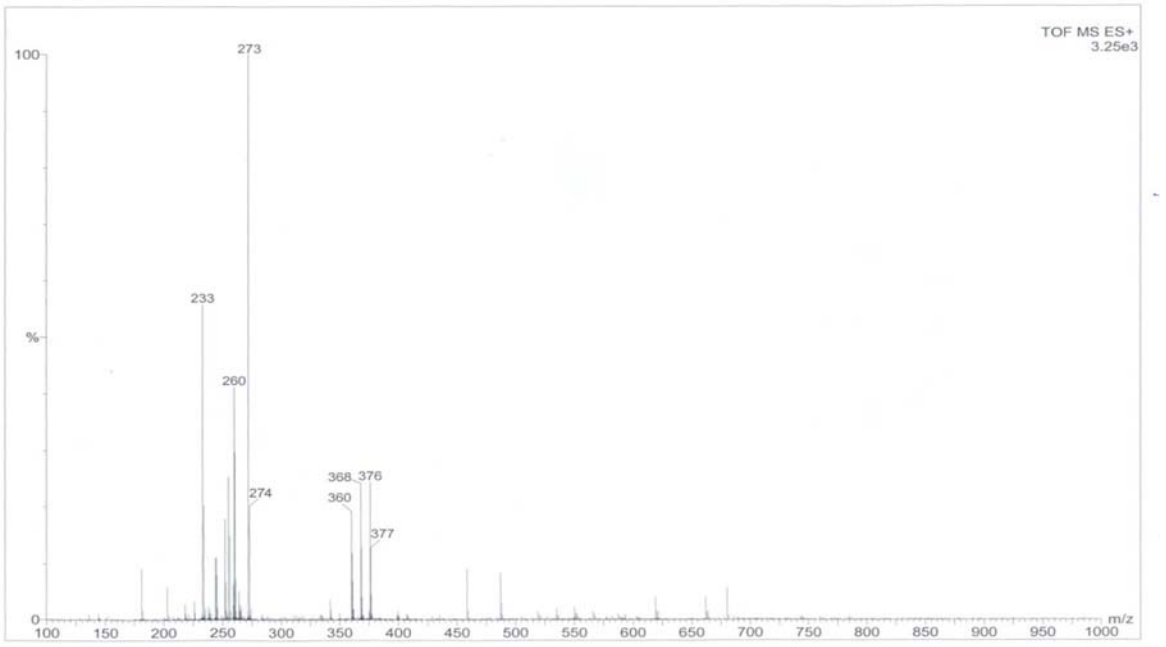


Fig. S2. ESI-MS spectrum of complex **2** in H_2O showing the parent ion peak at m/z 273 $(M-4ClO_4)^{4+}$.

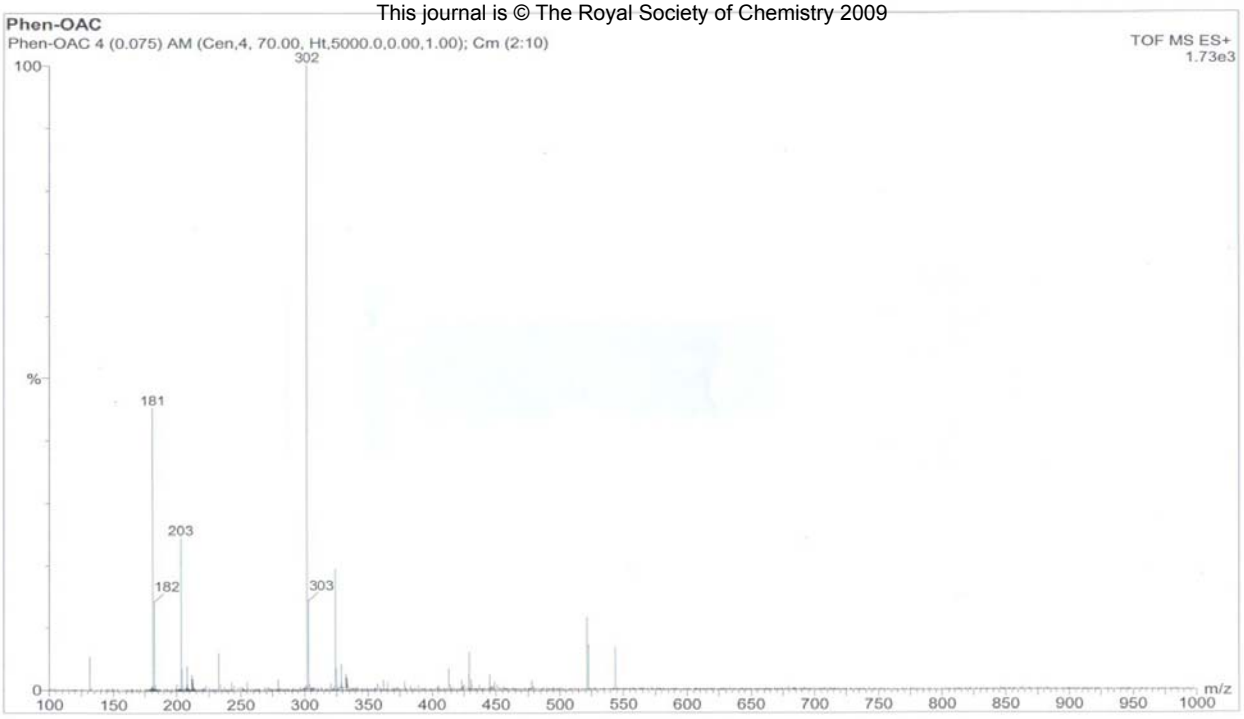


Fig. S3. ESI-MS spectrum of complex **3** in H_2O showing the parent ion peak at m/z 302 $(M-3ClO_4)^{3+}$.

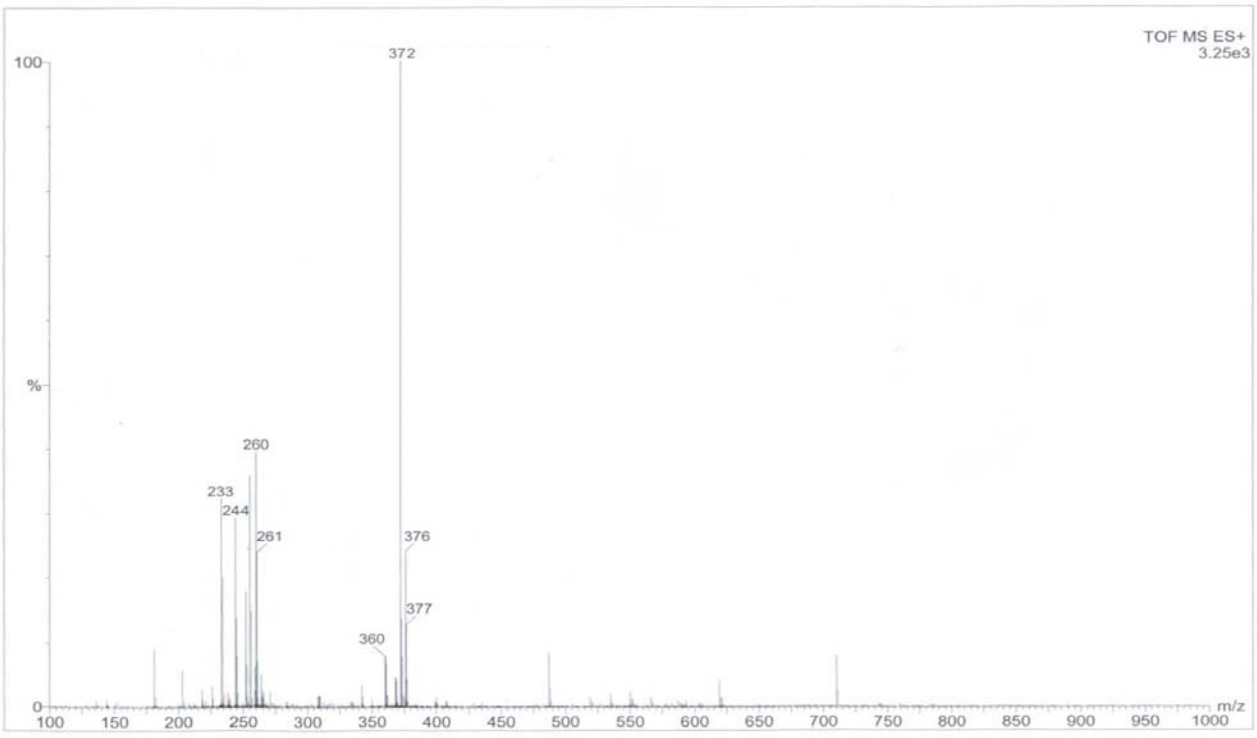


Fig. S4. ESI-MS spectrum of complex **4** in H_2O showing the parent ion peak at m/z 372 $(M-3ClO_4)^{3+}$.

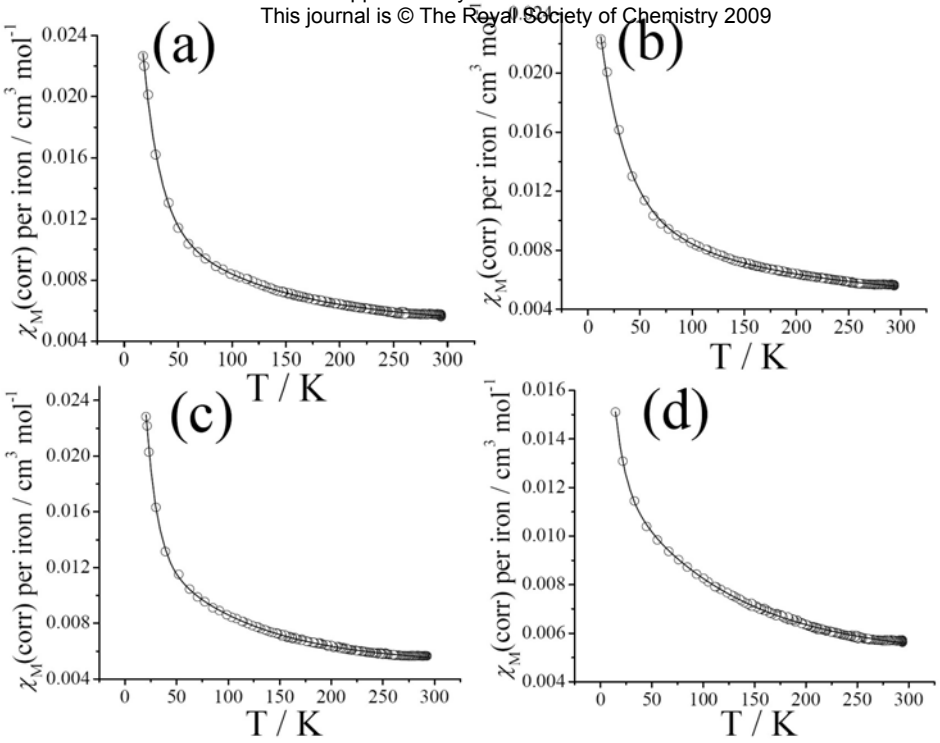


Fig. S5. Temperature dependence (295-18 K) of the molar magnetic susceptibility per iron(III) (circle) of the complexes **1** (a), **2** (b), **3** (c) and **4** (d). The solid lines represent the theoretical fits using the equation described in the text.

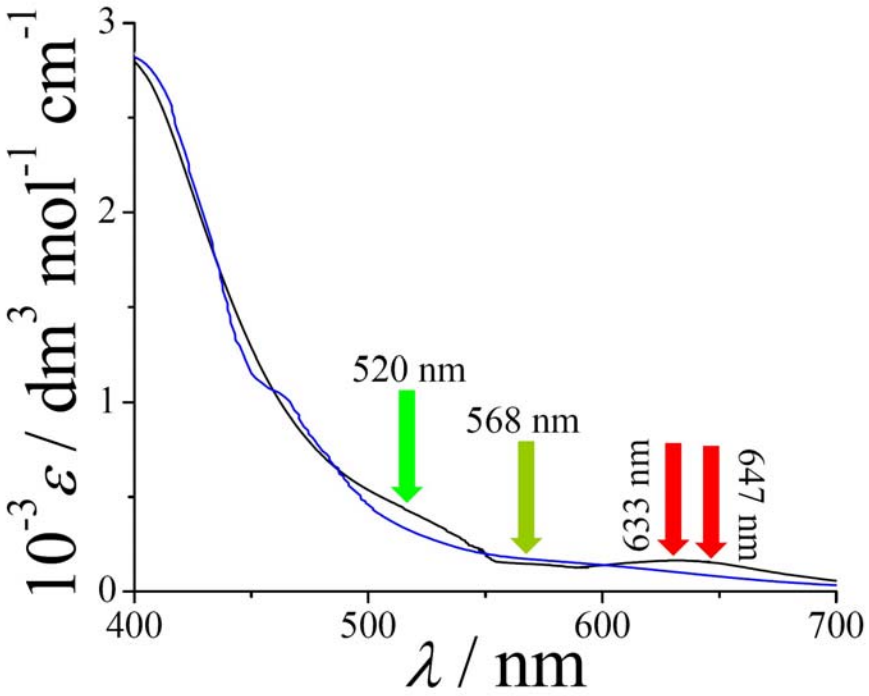


Fig. S6. The electronic spectra of the complexes **1**(—) and **3**(—) in Tris-HCl buffer showing the LMCT bands. The arrows indicate the wavelength of excitation used in the DNA cleavage experiment.

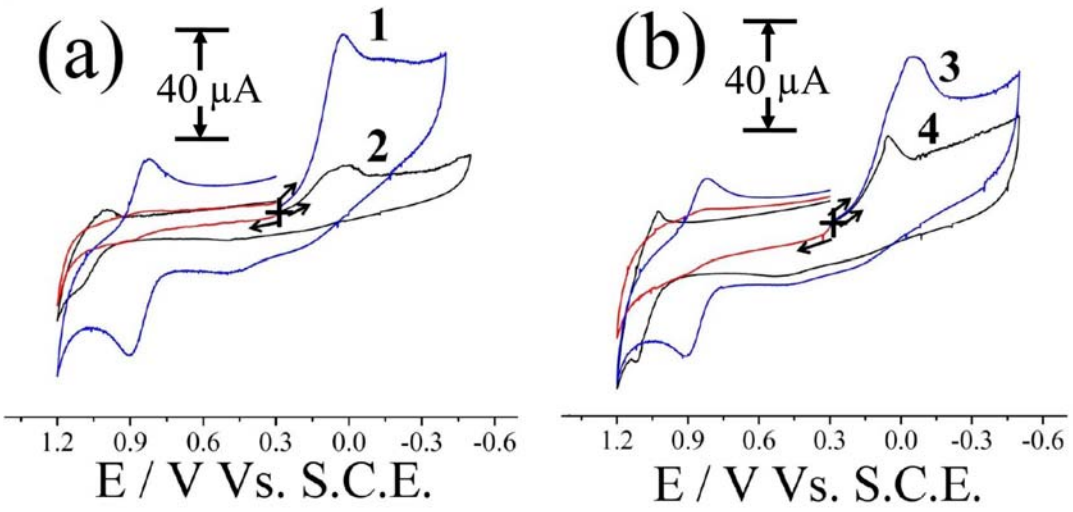


Fig. S7. The cyclic voltammetric responses of the complexes **1** and **2** (a) and **3** and **4** (b) in H_2O-0.1M KCl at a scan rate of 50 mV s^{-1} with reference to S.C.E. All the complexes display irreversible cyclic voltammetric response at ~100 mV with no anodic counterpart. The reversible voltammogram near 0.9 V is due to the formation of the binary complex of iron(II), viz. $[Fe(phen)_3]^{2+}$ or $[Fe(dpq)_3]^{2+}$ from degradation of diiron species. This voltammogram is not visible during only anodic scan (red line).

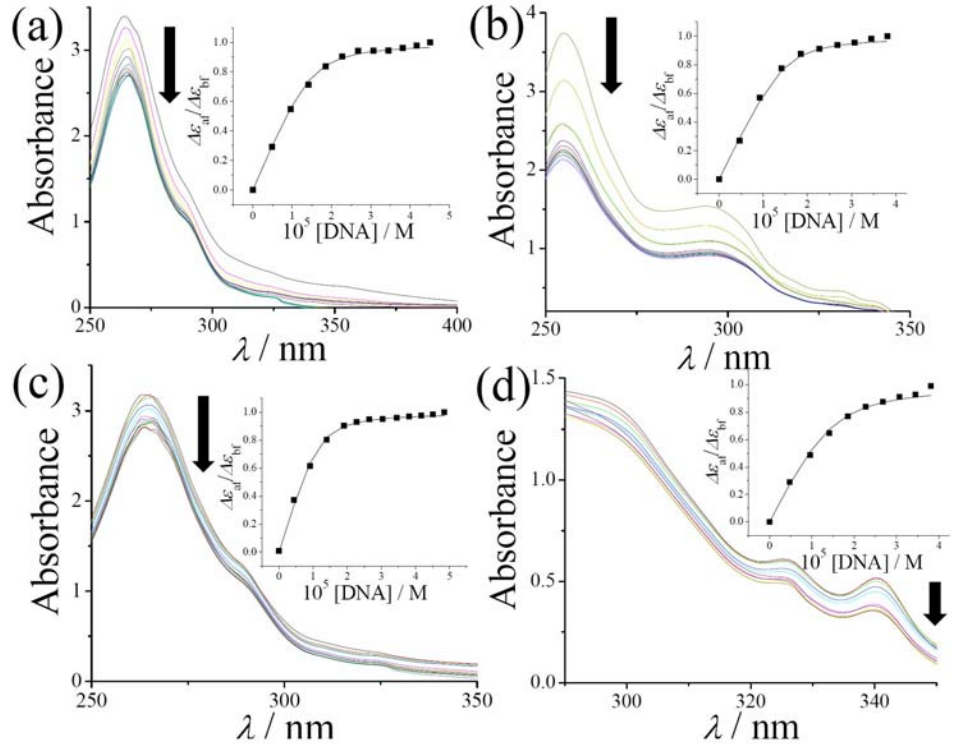
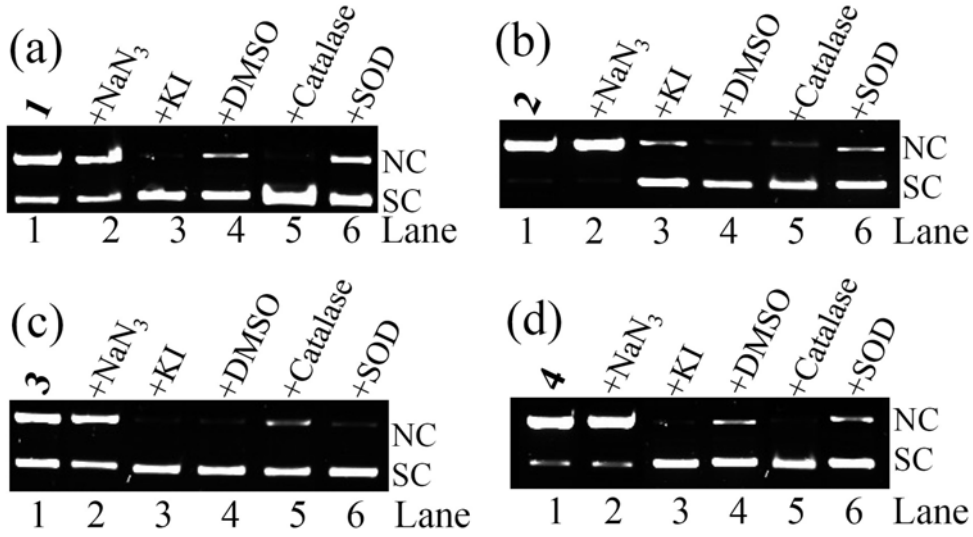
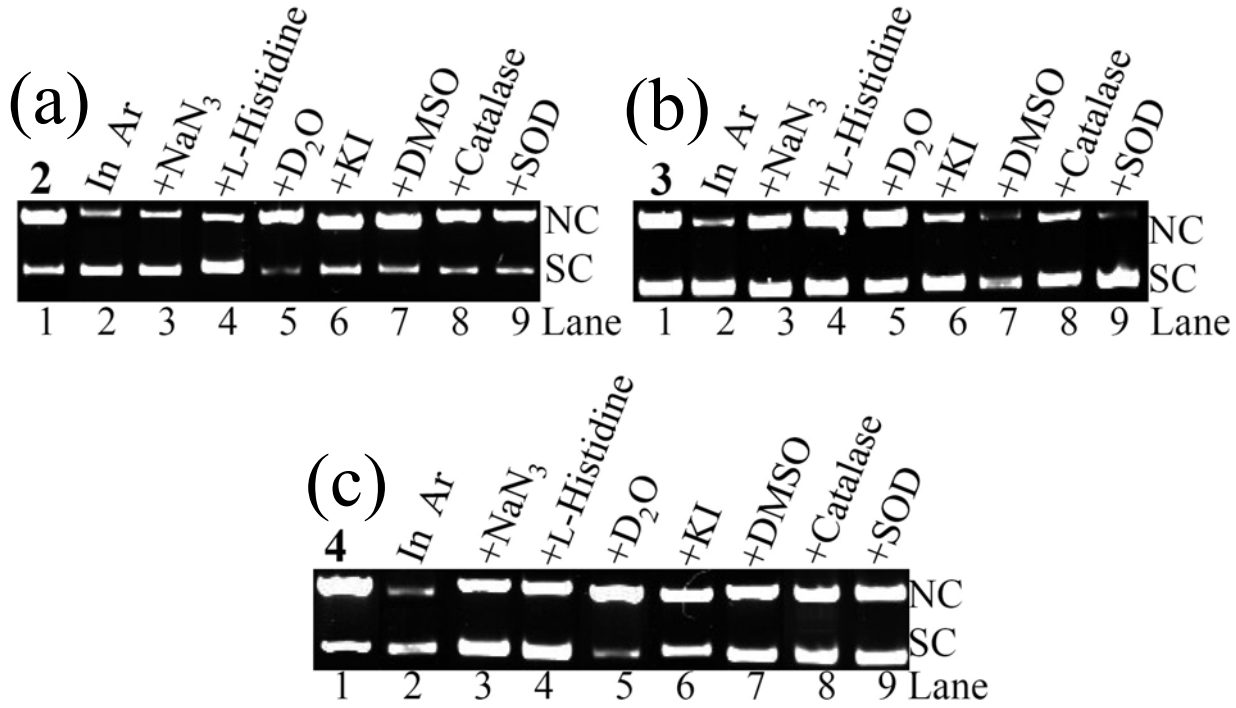


Fig. S8. Spectral traces showing the effect of addition of CT DNA (250 μM NP) to a 30 μM complex **1** (a), **2** (b), **3** (c) and 4 (d) in Tris-HCl buffer (pH 7.2) with the insets showing the MvH plots ($\Delta\varepsilon_{af}/\Delta\varepsilon_{bf}$ vs.[DNA]). The experimental details are given in the text.



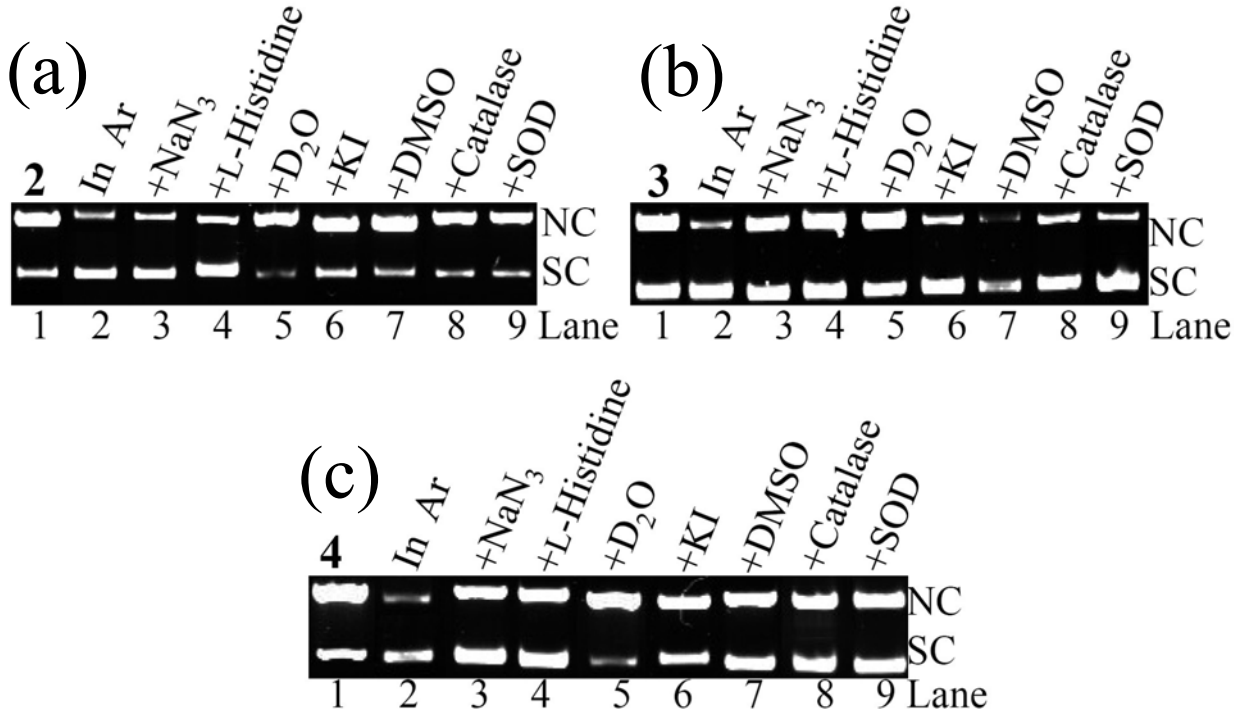
Complex + MPA (Fig.)	%NC form (Chemical Nuclease Activity)					
	Complex + MPA	+ NaN_3[a]	+ KI[b]	+ DMSO[c]	+ Catalase[d]	+ SOD[e]
1 + MPA (S9a)	63	60	9	19	11	27
2 + MPA (S9b)	96	94	25	8	8	18
3 + MPA (S9c)	53	55	6	5	15	7
4 + MPA (S9d)	84	80	14	18	7	18

Fig. S9. The gel electrophoresis diagram showing the mechanistic aspects of chemical oxidation of SC pUC19 DNA (0.2 μg, 30 μM) by the complexes (**1** – **4**) in the presence of the various additives in 50 mM Tris-HCl/NaCl buffer (pH 7.2) in the presence of 3-mercapto propionic acid (MPA) as a reducing agent. The percent of cleavage in the presence of various additives are tabulated. Complex concentration = 30 μM. The %NC for DNA control is ~3%. [a][NaN_3] = 500 μM. [b][KI] = 500 μM. [c]DMSO = 6 μL. [d]SOD = 2 units. [e]Catalase = 2 units.



Complex (Fig.)	% NC form (photo-irradiation at 365 nm)								
	Complex	+ NaN_3[a]	+ L-Histidine[b]	+ D_2O[c]	+ KI[d]	In Argon	+ DMSO[e]	+Catalase[f]	+SOD[g]
2 (S10a)	83	21	17	90	84	24	85	87	80
3 (S10b)	67	70	72	68	10	20	15	15	18
4 (S10c)	96	48	53	91	64	25	50	56	71

Figure S10. The gel electrophoresis diagram showing the mechanistic aspects of photocleavage of SC pUC19 DNA (0.2 μg, 30 μM) by the complexes in the presence of the various additives in 50 mM Tris-HCl/NaCl buffer (pH 7.2) on photoexposure of UV light of 365 nm. The percent of cleavage in the presence of various additives are tabulated. Complex concentration = 5.5 μM. The exposure time for the complexes is 2 h. The %NC for DNA control is ~2%. [a][NaN_3] = 200 μM. [b][L-His] = 200 μM. [c]D_2O = 16 μL. [d][KI] = 200 μM. [e]DMSO = 6 μL. [f]SOD = 2 units. [g]Catalase = 2 units.



Complex (Fig.)	% NC form (photo-irradiation in visible light)								
	Complex	In Argon	+ NaN_3[a]	+L-Histidine[b]	+D_2O[c]	+KI[d]	+DMSO[e]	+Catalase[f]	+SOD[g]
2 (S11a)	78	26	31	25	88	80	76	80	78
3 (S11b)	70	22	68	72	74	21	15	19	22
4 (S11c)	88	25	56	57	95	49	52	47	53

Figure S11. The gel electrophoresis diagram showing the mechanistic aspects of the photocleavage of SC pUC19 DNA (0.2 μg, 30 μM) by the complexes in the presence of the various additives in 50 mM Tris-HCl/NaCl buffer (pH 7.2) on irradiation with light of λ = 520 nm for **2** and **4,** λ = 647 nm for **3**. [complex] = 60 μM. The exposure time is 2 h. [a][NaN_3] = 500 μM, [b][L-His] = 500 μM, [c]D_2O = 16 μM, [d][KI] = 500 μM, [e]DMSO = 6 μL, [f]Catalase = 4 units. [g]SOD = 4 units.