ELECTRONIC SUPPLEMENTARY MATERIALS

Efficient hydrolytic cleavage of plasmid DNA by chloro-cobalt(II) complexes based on sterically hindered pyridyl tripod tetraamine ligands: synthesis, crystal structure and DNA cleavage activity[†]

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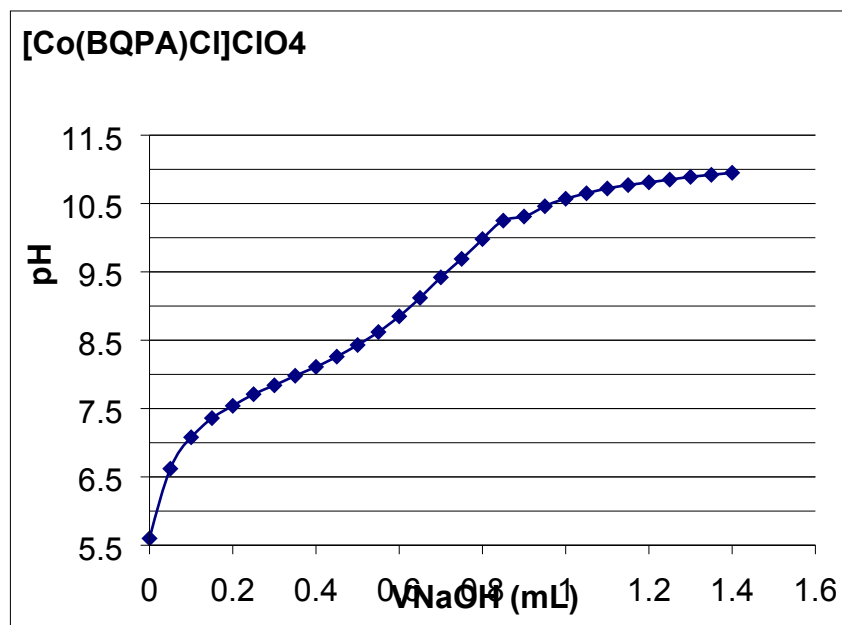
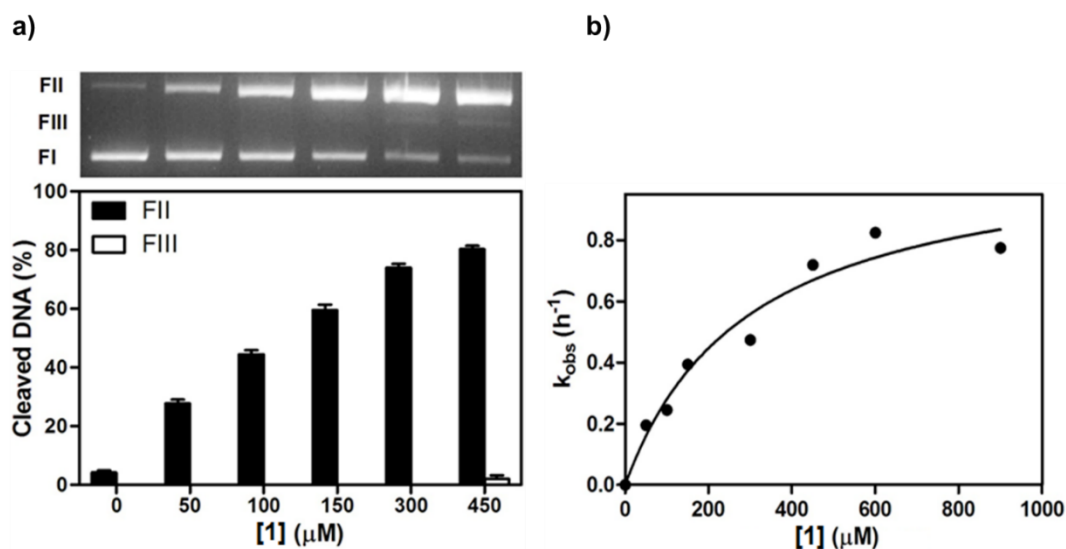**Fig. S1.** Potentiometric pH titration of $[Co(BQPA)(H_2O)]^{2+}$ (4.0 x 10^{-3}M) with standard 0.05 M NaOH at 37 °C .

Fig. S2. (**a**) Agarose gel electrophoresis pattern and the corresponding plots for the cleavage of pBSK II plasmid DNA (~ 25 μM) by complex **1** at different complex concentrations (50-450 μM) at pH 7.0 Tris-HCl buffer (10 mM) and 37 °C; t = 2 h. Results are expressed as mean standard deviation (n = 3). (**b**) *Pseudo* Michaelis-Menten kinetics of the cleavage of pBSK II plasmid DNA (~ 25 μM), [**1**] = 50-900 μM, pH 7.0 Tris-HCl buffer (10 mM) and 37 °C**.**
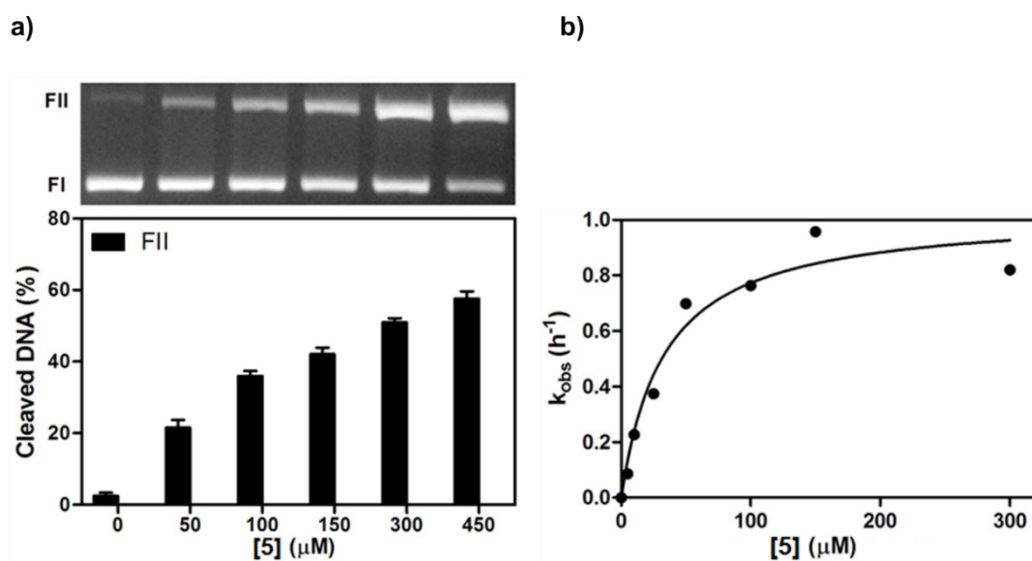
Fig. S3. (a) Agarose gel electrophoresis pattern and the corresponding plots for the cleavage of pBSK II plasmid DNA (~ 25 μM) by complex **5** at different complex concentrations (50-450 μM) at pH 7.0 Tris-HCl buffer (10 mM) and 37 °C; t = 2 h. Results are expressed as mean standard deviation (n = 3). **(b)** *Pseudo* Michaelis-Menten kinetics of the cleavage of pBSK II plasmid DNA (~ 25 μM), [**5**] = 5-300 μM, pH 7.0 Tris-HCl buffer (10 mM) and 37 °C.
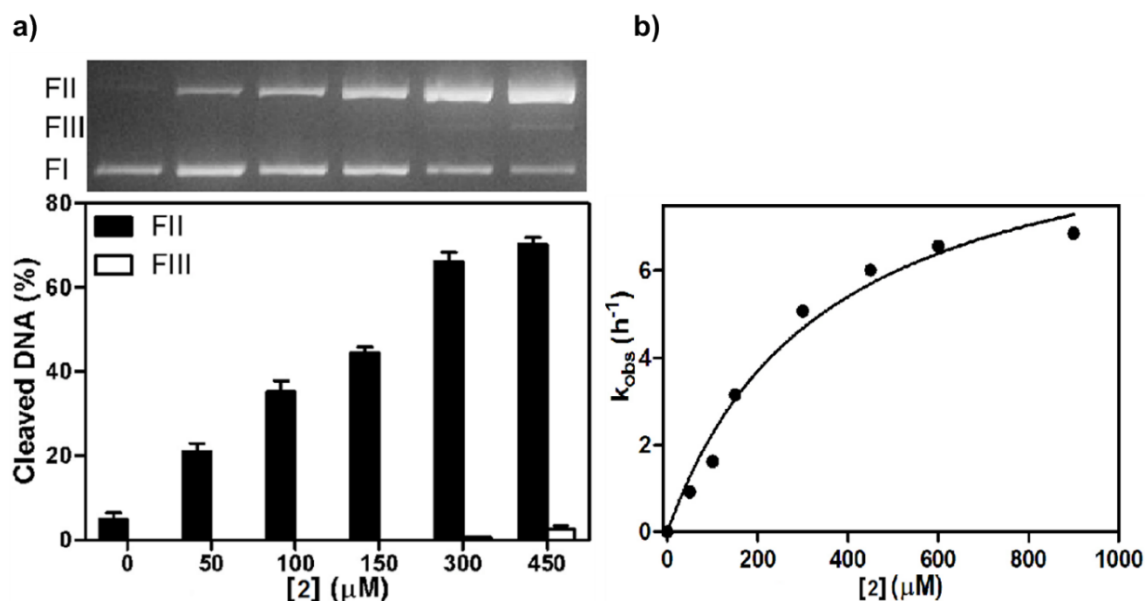
Fig. S4. (a) Agarose gel electrophoresis pattern and the corresponding plots for the cleavage of pBSK II plasmid DNA (~ 25 μM) by complex **2** at different complex concentrations (50-450 μM) at pH 9.0 Tris-HCl buffer (10 mM) and 37 °C; t = 15 min. Results are expressed as mean standard deviation (n = 3). **(b)** *Pseudo* Michaelis-Menten kinetics of the cleavage of pBSK II plasmid DNA (~ 25 μM), [**2**] = 50-900 μM, pH 9.0 Tris-HCl buffer (10 mM) and 37 °C**.**

Fig. S5. (a) Agarose gel electrophoresis pattern and the corresponding plots for the cleavage of pBSK II plasmid DNA (~ 25 μM) by complex **3** at different complex concentrations (50-450 μM) at pH 9.0 Tris-HCl buffer (10 mM) and 37 °C; time = 30 min. Results are expressed as mean standard deviation (n = 3). **(b)** *Pseudo* Michaelis-Menten kinetics of the cleavage of pBSK II plasmid DNA (~ 25 μM), [**2**] = 50-900 μM, pH 9.0 Tris-HCl buffer (10 mM) and 37 °C**.**

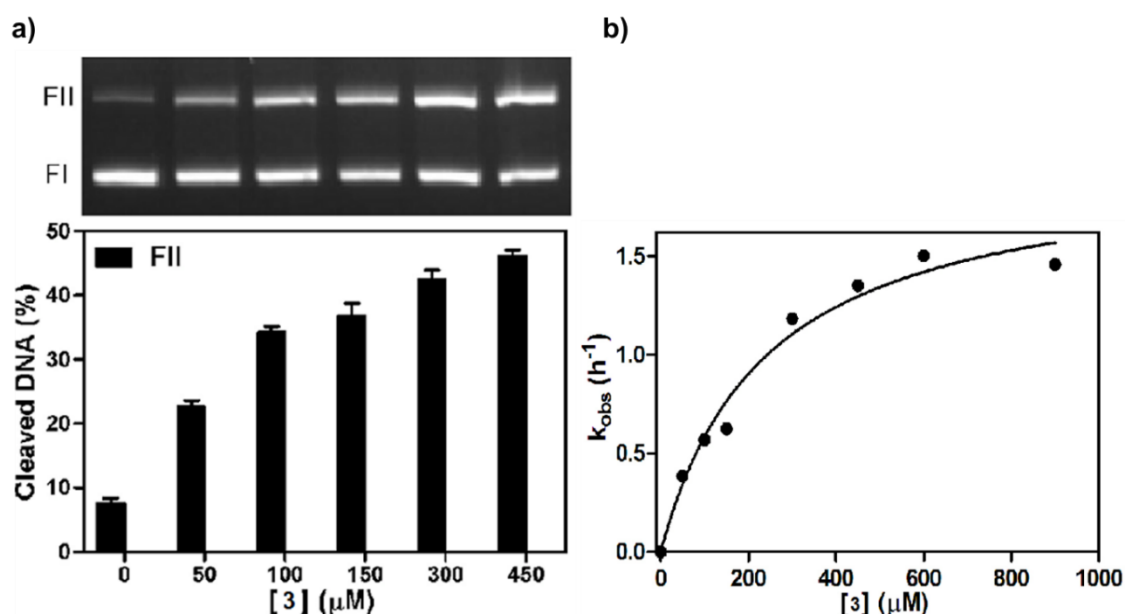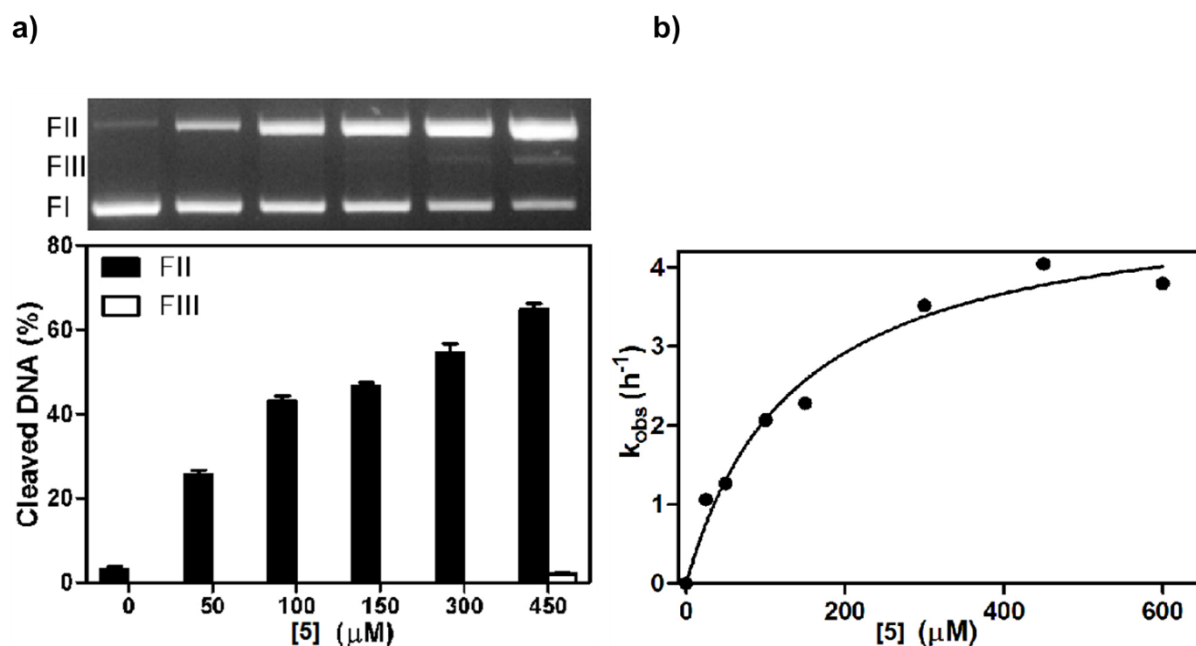**Fig. S6. (a)** Agarose gel electrophoresis pattern and the corresponding plots for the cleavage of pBSK II plasmid DNA (~ 25 μM) by complex **5** at different complex concentrations (50-450 μM) at pH 9.0 Tris-HCl buffer (10 mM) and 37 °C; time = 30 min. Results are expressed as mean standard deviation (n = 3). **(b)** *Pseudo* Michaelis-Menten kinetics of the cleavage of pBSK II plasmid DNA (~ 25 μM), [**5**] = 50-600 μM, pH 9.0 Tris-HCl buffer (10 mM) and 37 °C.
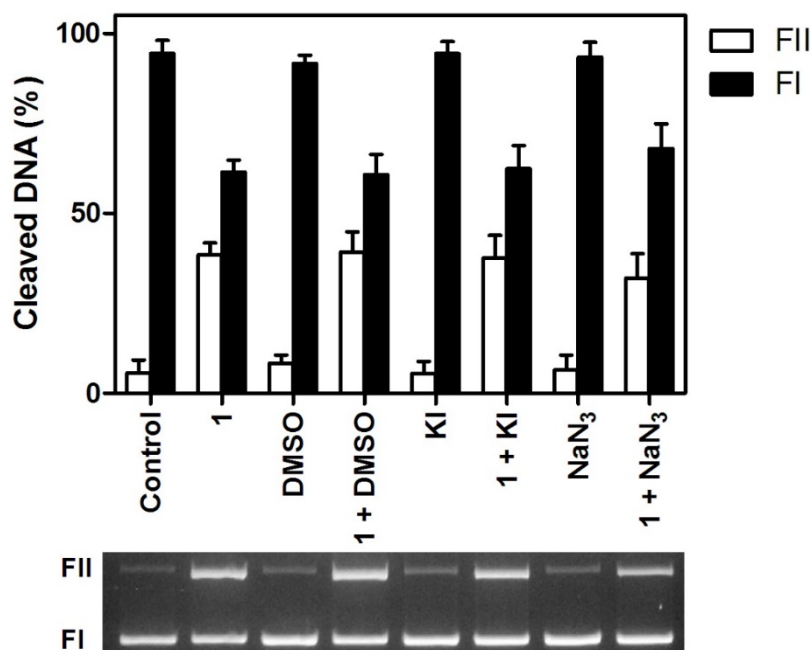
Fig. S7. Cleavage of pBSK II plasmid DNA ([DNA] = ~25 μM) by **1** ([**1**] = 450 μM) in the presence and absence of ROS scavengers. Reaction Conditions: [Buffer] = 10 mM Tris-HCl pH 7.0, 37 °C, t = 30 min., [DMSO] = 0.5 M, [KI] = 0.4 mM, [NaN$_3$] = 0.5 mM. Results are expressed as mean ± standard deviation (n = 3).

Fig. S8. Cleavage of pBSK II plasmid DNA (~25 μM) by **2** (450 μM) in the presence and absence of ROS scavengers. Reaction Conditions: [Buffer] = 10 mM Tris-HCl pH 7.0, 37 °C, t = 30 min, [DMSO] = 0.5 M, [KI] = 0.4 mM, [NaN$_3$] = 0.5 mM. Results are expressed as mean ± standard deviation (n = 3).
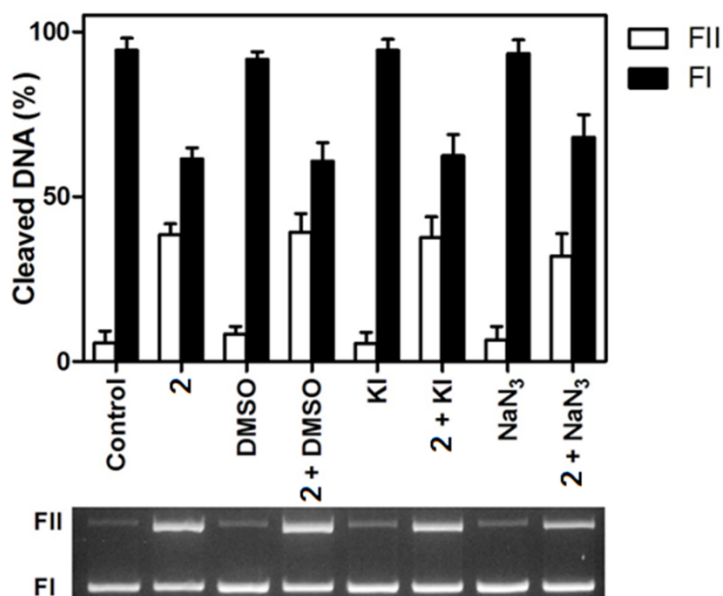
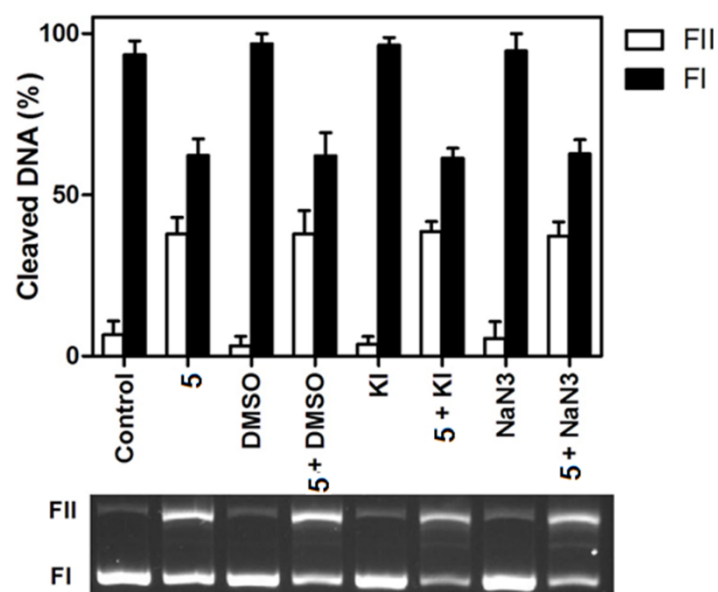**Fig. S9.** Cleavage of pBSK II plasmid DNA (~25 μM) by **5** (450 μM) in the presence and absence of ROS scavengers. Reaction Conditions: [Buffer] = 10 mM Tris-HCl pH 7.0, 37 °C, t = 30 min, [DMSO] = 0.5 M, [KI] = 0.4 mM, [NaN$_3$] = 0.5 mM. Results are expressed as mean ± standard deviation (n = 3).

Fig. S10. Cleavage of Oligo1 (49-mer) oligonucleotide by complex ions [Co(6-MeTPA)Cl]$^+$ and [Co(BPQA)Cl]$^+$. Lanes labeled as Control, A+G and DNAse I represent a sample without treatment, the Maxam-Gilbert Guanine + Adenine ladder and a sample partially digested by DNAse I. Note the asterisk (*) at cleavage product with terminal Adenine 12: the fragment of G+A ladder (3'-phosphate termini) migrates slower than the corresponding in the DNAse I digestion (3'-OH) due to the termini composition.

Fig. S11. Cleavage of pBSK II plasmid DNA (~25 μM) by **1** (450 μM) in the presence of DNA groove binders distamycin and methyl green (MG) [Distamycin or MG] = 50 μM). Reaction Conditions: [Buffer] = 10 mM Tris-HCl pH 7.0, 37 °C, t = 30 min. Results are expressed as mean ± standard deviation (n = 3).
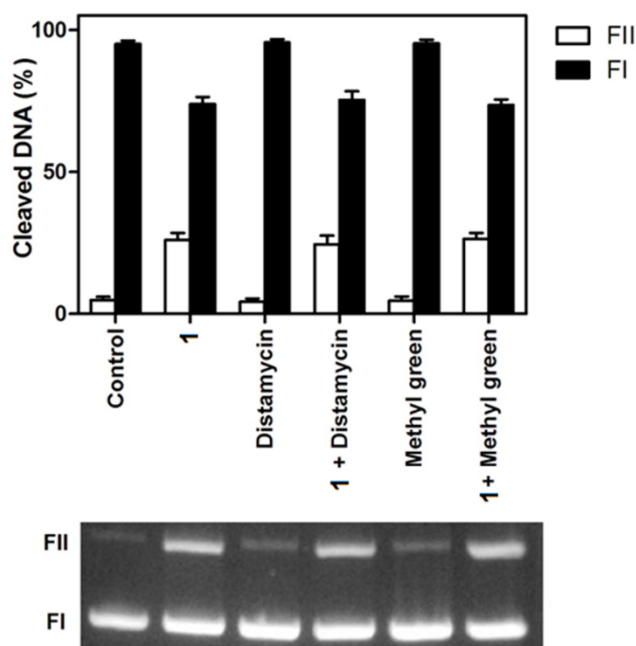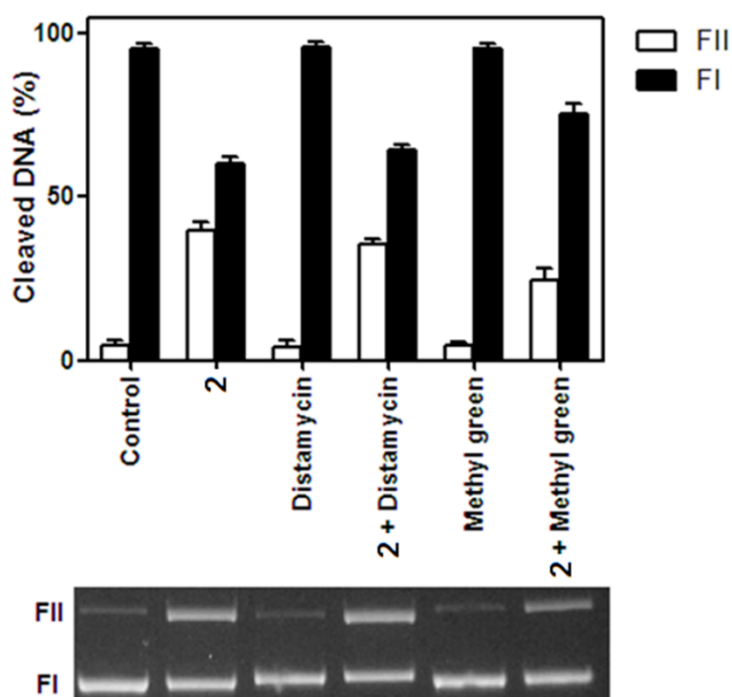

Fig. S12. Cleavage of pBSK II plasmid DNA (~25 μM) by **2** (450 μM) in the presence of DNA groove binders distamycin and methyl green (MG) [Distamycin or MG] = 50 μM). Reaction Conditions: [Buffer] = 10 mM Tris-HCl pH 7.0, 37 °C, t = 30 min. Results are expressed as mean ± standard deviation (n = 3).

Fig. S13. Cleavage of pBSK II plasmid DNA (~25 μM) by **3** (450 μM) in the presence of DNA groove binders distamycin and methyl green (MG) [Distamycin or MG] = 50 μM). Reaction Conditions: [Buffer] = 10 mM Tris-HCl pH 7.0, 37 °C, t = 30 min. Results are expressed as mean ± standard deviation (n = 3).
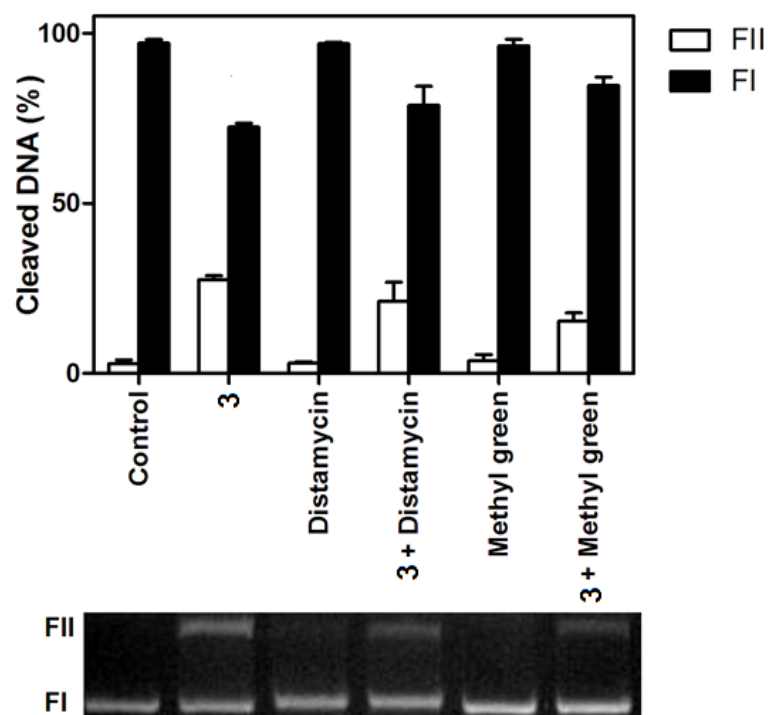
Table S1. *Pseudo*-Michael-Menten Kinetics of pBSK II Plasmid DNA Cleavage by Chloro-cobalt(II) Complexes **1-5** at Different Complex Concentrations, [DNA] ≈ 25 μM, [buffer] = 10 mM Tris-HCl pH 9.0 and 37 °C.

Complex	[Co(II)] (μM)	k_{obs} (h^{-1})	k_{cat} (h^{-1}) [a]	K_M (M)
[Co(TPA)Cl]ClO$_4$ **(1)**	5	0.232	3.02	3.64 x 10^{-5}
	10	0.732		
	15	0.810		
	30	1.41		
	50	1.78		
	100	2.17		
	150	2.43		
[Co(6-MeTPA)Cl]ClO$_4$ **(2)**	50	0.924	10.1	3.47 x 10^{-4}
	100	1.62		
	150	3.15		
	300	5.08		
	450	6.02		
	600	6.56		
	900	6.86		
[Co(6-Me$_2$TPA)Cl]ClO$_4$ **(3)**	50	0.385	1.99	2.40 x 10^{-4}
	100	0.569		
	150	0.624		
	300	1.18		
	450	1.35		
	600	1.50		
	900	1.46		
[Co(BPQA)Cl]ClO$_4$ **(4)**	50	2.61	16.8	3.65 x 10^{-4}
	100	3.89		
	150	5.09		
	300	6.66		
	450	9.72		
	600	10.2		
	900	12.3		
[Co(BQPA)Cl]ClO$_4$ **(5)**	25	1.06	4.92	1.37 x 10^{-4}
	50	1.27		
	100	2.07		
	150	2.28		
	300	3.52		
	450	4.04		
	600	3.79		

[a] k_{cat} represents the maximum rate of cleavage at the saturation ($V_{max} = k_{cat}$)