

Supporting Information for

**An Effective Approach to Artificial Nucleases Using
Copper(II) Complexes Bearing Nucleobases**

Jin-Tao Wang, Xiao-Hui Zheng, Huo-Yan Chen, Hui Chao, Zong-Wan Mao, and Liang-Nian Ji*

MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical
Engineering, Sun Yat-Sen University, Guangzhou 510275, China.

* Corresponding author. Tel.: +86 20 84113788; Fax: +86 20 84112245.

E-mail address: cesmzw@mail.sysu.edu.cn

Contents

Fig. S1. ^1H NMR spectra of L^1 - L^3 .

Fig. S2. ^{13}C NMR spectra of L^1 - L^3 .

Fig. S3. ESI-MS spectra of L^1 - L^3 .

Fig. S4. ESI-MS spectra of **1-3**.

Fig. S5. X-Band ESR spectra of complexes **1-3** at 110k.

Fig. S6. Molecular modeling of copper(II) complexes. Molecular representations of complexes **1-3** were determined by B3LYP/6-31G(d, p) geometry optimizations. Atoms are labeled and hydrogen atoms are omitted for clarity.

Table S1. Selected bond lengths (Å) and angles (°) for **1-3**.

Fig. S7. Circular dichroism (CD) spectra of pBR322 DNA (25×10^{-6} M bp) modified by bpy at different ligand-to-DNA ratios. DNA was modified by bpy at $r_b = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$.

Table S2 Statistical Efficiency of Single-Strand and Double-Strand Break Formation by complex **3**.

Fig. S8. Ionic strength dependence of the plasmid DNA (38 μM bp) cleavage by **1-3** at 37 °C in 20 mM HEPES at pH 7.5. (a) 70 μM **1** for 24 min; lane1, DNA control; lanes 2-11, DNA + **1** with 0, 10, 20, 40, 70, 100, 150, 200, 300 and 400 mM NaCl; (b) 70 μM **2** for 6 min; lane1, DNA control; lanes 2-11, DNA + **2** with 0-400 mM NaCl; (c) 70 μM **3** for 40 min; lane1, DNA control; lanes 2-11, DNA + **3** with 0-400 mM NaCl.

Fig. S9. Agarose gel electrophoresis and corresponding time course plots showing cleavage of pBR322 DNA by **1** and **2** (10-250 μM) in 20 mM pH 7.5 HEPES buffer at 37 °C. In plans, lane C means DNA control. In graphs, symbol ■ indicates the experimental data for the SC forms. The lines connecting them are single exponential fits.

Fig. S10. DNA cleavage under “true” Michaelis-Menten kinetic conditions in which the concentration of complex **1** is kept constant at 100 μM and the DNA concentration is varied from 19-190 μM in 20 mM pH 7.5 HEPES buffer at 37 °C.

Fig. S11. Agarose gel showing cleavage of 38 μM bp pBR322 DNA incubated with L^1 (100 μM bp) for 1 h (lane 2), L^2 (100 μM) for 1 h (lane 3), L^3 (100 μM) for 1h (lane 4), CuCl_2 (200 μM) for 2 h (lane 5) and DNA control (lane 1) in 20 mM HEPES, pH 7.5 at 37 °C.

Fig. S12. View of **4** binding with the d(CGCGAATTCGCG)₂.

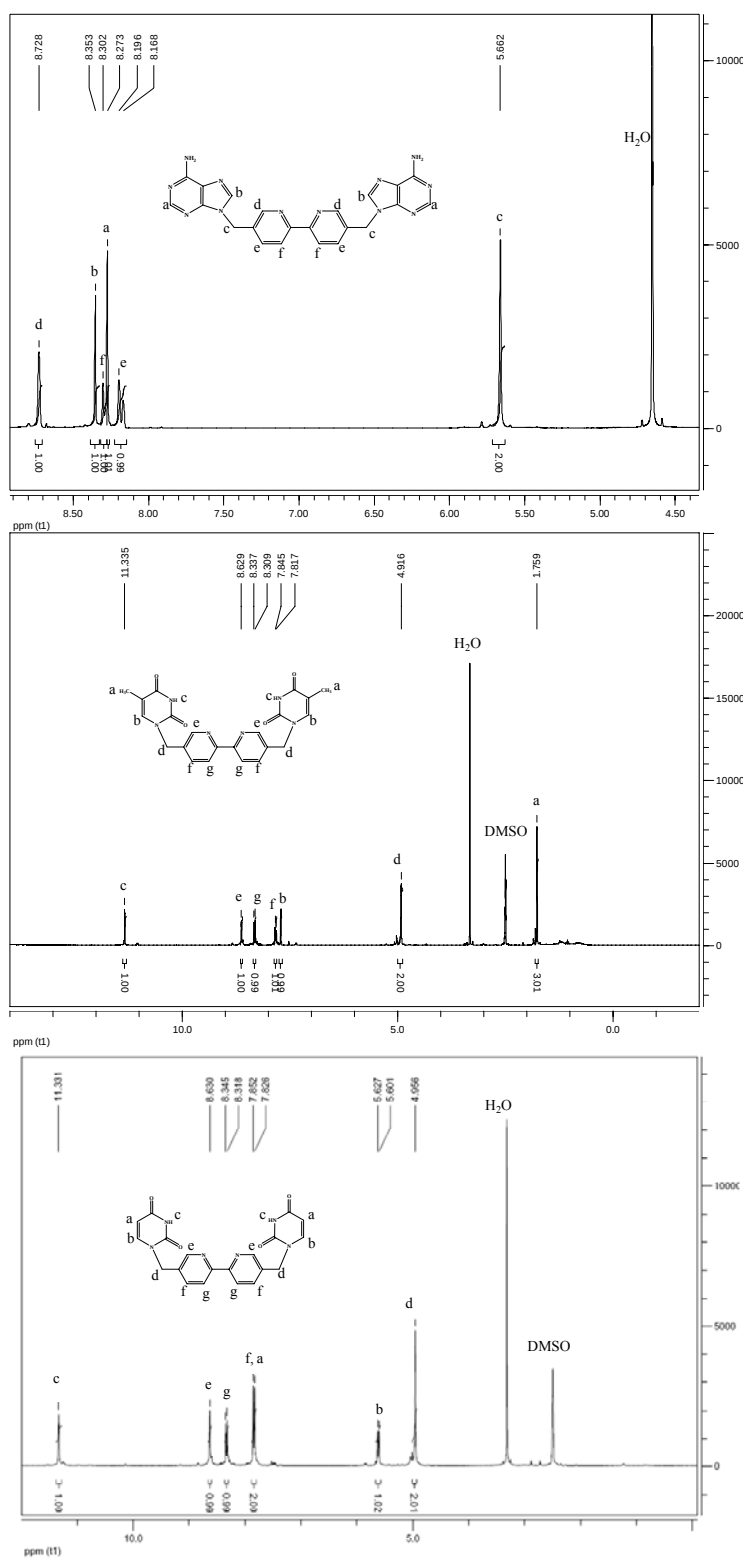


Fig. S1.

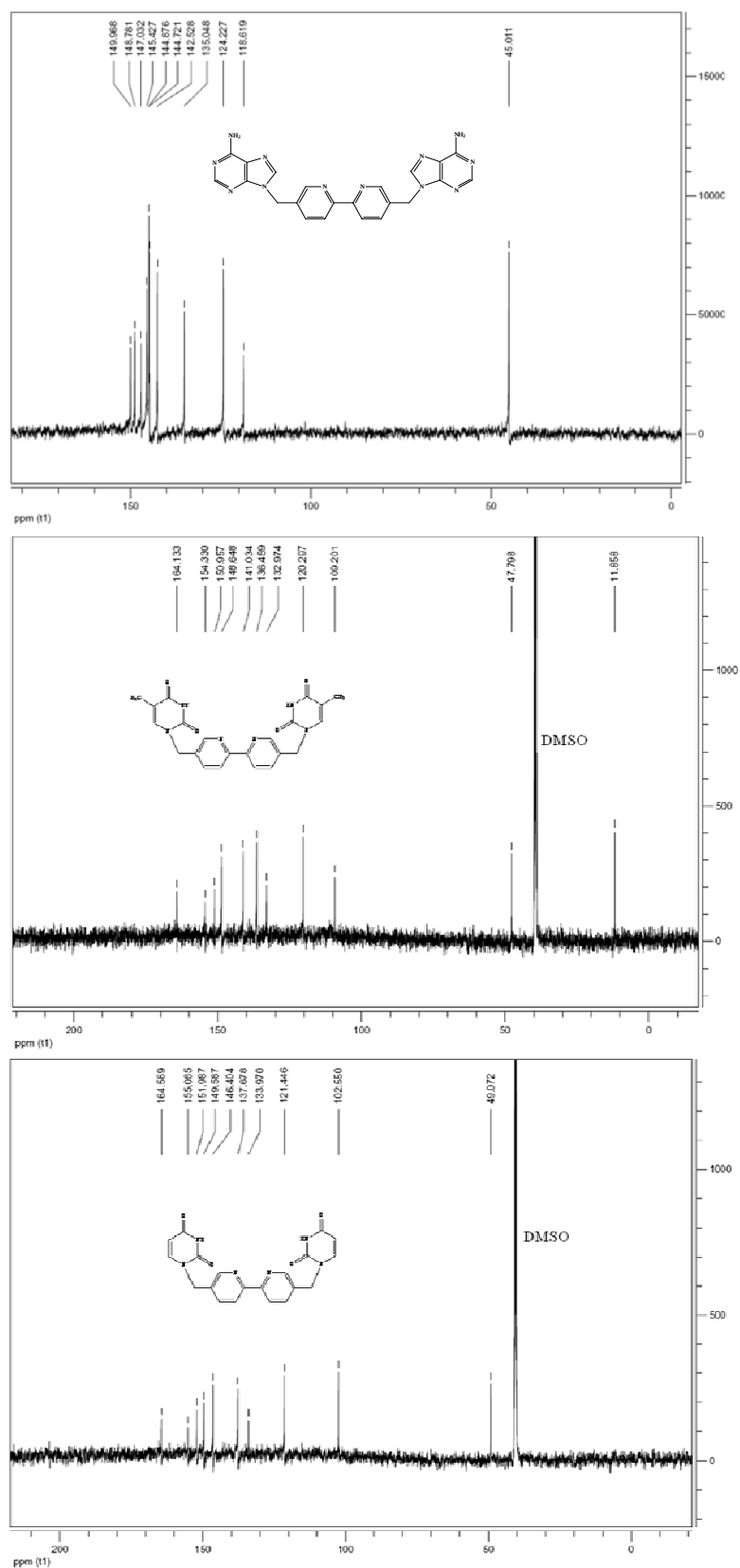


Fig. S2.

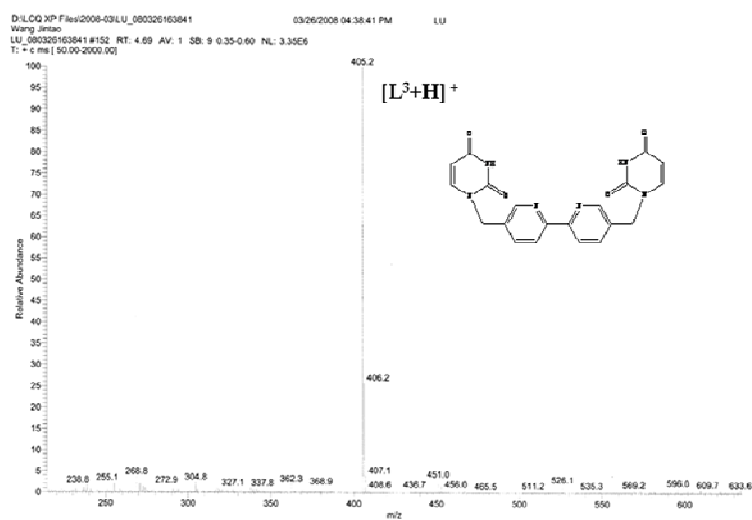
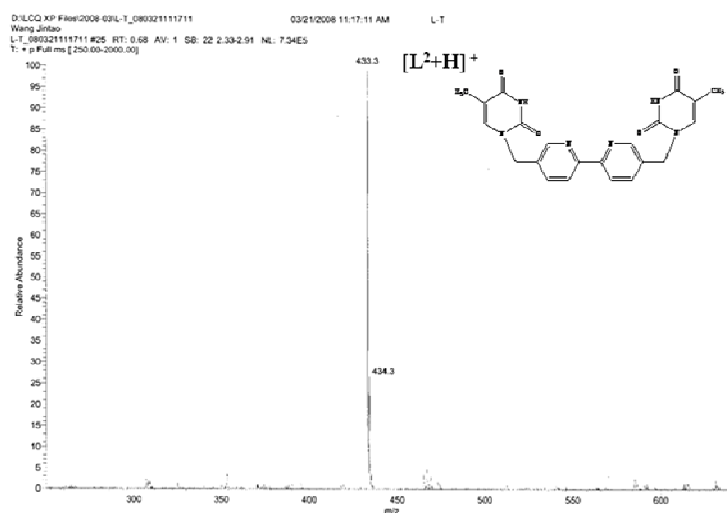
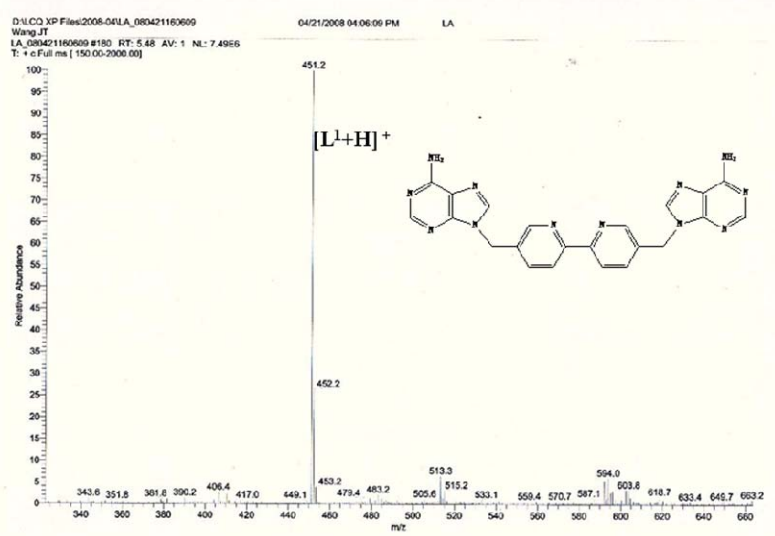
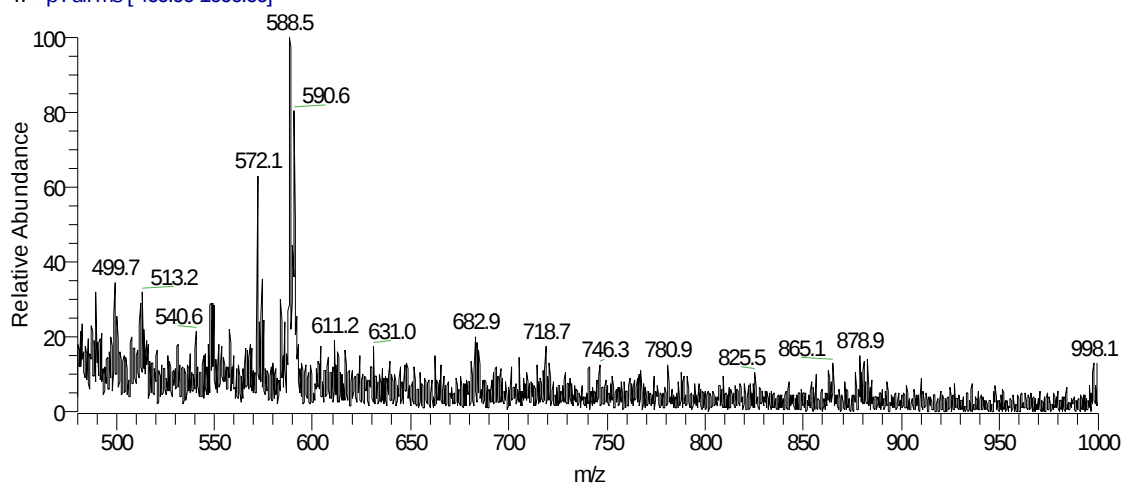


Fig. S3.

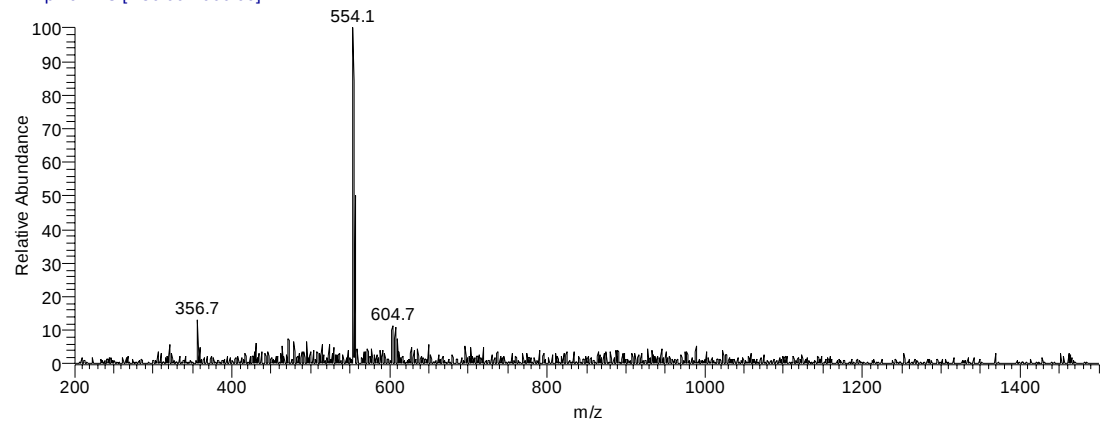
4#146 RT: 3.44 AV: 1 NL: 1.35E5

T: +p Full ms [460.00-1000.00]



LTCu #27 RT: 0.75 AV: 1 SB: 9 0.21-0.44 NL: 1.05E6

T: +p Full ms [150.00-2000.00]



UCu #26 RT: 0.44 AV: 1 SB: 19 0.03-0.34 NL: 4.35E6

T: +c Full ms [200.00-1000.00]

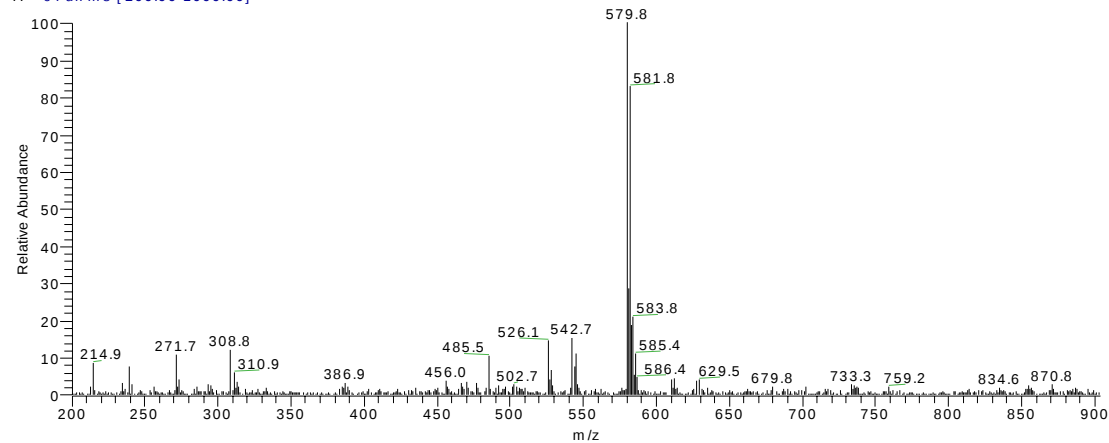


Fig. S4.

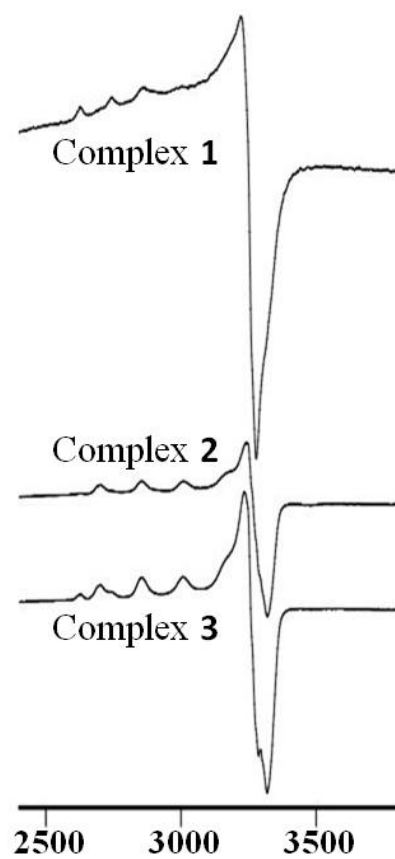


Fig. S5.

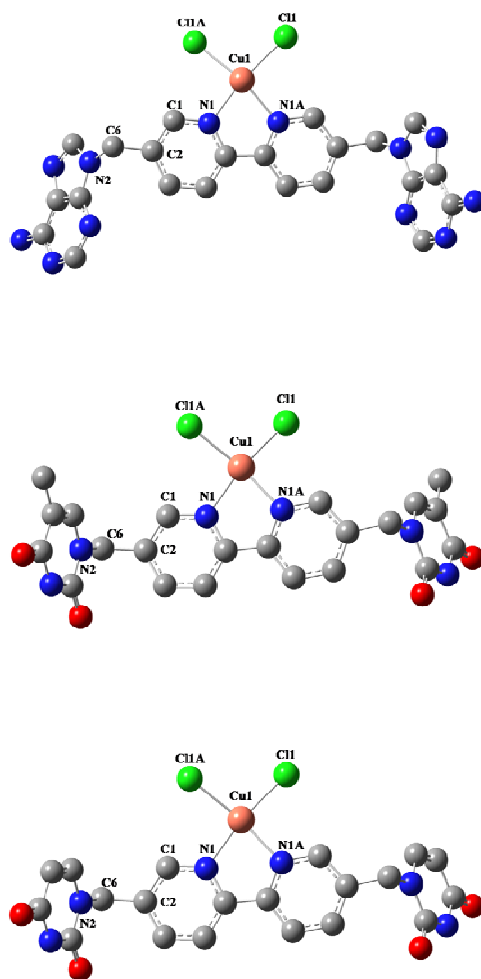


Fig. S6.

Table S1.

	Complex 1	Complex 2	Complex 3
Cu(1)-N(1)	2.08	2.08	2.08
Cu(1)-N(1A)	2.08	2.08	2.08
Cu(1)-Cl(1)	2.29	2.29	2.29
Cu(1)-Cl(1A)	2.29	2.29	2.29
C(1)-N(1)	1.35	1.35	1.35
C(6)-C(2)	1.52	1.52	1.52
C(6)-N(2)	1.47	1.49	1.49
N(1)-Cu(1)-N(1A)	78.64	78.67	78.60
N(1A)-Cu(1)-Cl(1)	93.65	93.71	93.66
Cl(1)-Cu(1)-Cl(1A)	97.39	98.20	98.01
N(1)-Cu(1)-Cl(1A)	93.65	93.71	93.66
N(1)-Cu(1)-Cl(1)	163.23	161.47	162.06
N(1A)-Cu(1)-Cl(1A)	163.23	161.46	162.07
C(1)-C(2)-C(6)	120.39	120.17	120.12
C(2)-C(6)-N(2)	113.35	112.87	112.97

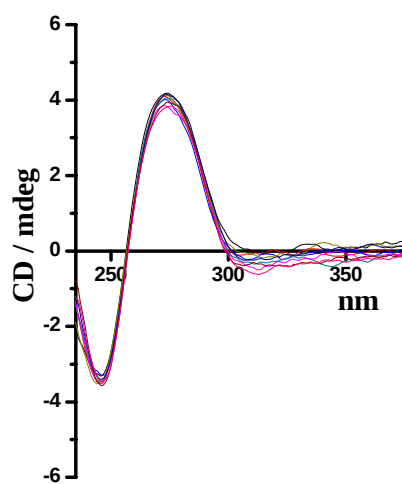


Fig. S7.

Table S2.

Complex 3 (μM)	Reaction time (min)	Fraction of DNA			<i>n</i> 1	<i>n</i> 2	<i>n</i> 1/ <i>n</i> 2
		Supercoiled	Nicked	Linear			
50	10	0.296	0.680	0.024	1.193	0.025	48.099
50	20	0.207	0.734	0.059	1.512	0.063	24.173
70	28	0.185	0.745	0.071	1.615	0.076	21.232
70	35	0.447	0.531	0.022	0.784	0.023	34.655
70	42	0.327	0.596	0.077	1.037	0.083	12.512
250	12	0.282	0.675	0.044	1.223	0.046	26.855
250	18	0.150	0.745	0.105	1.786	0.117	15.258

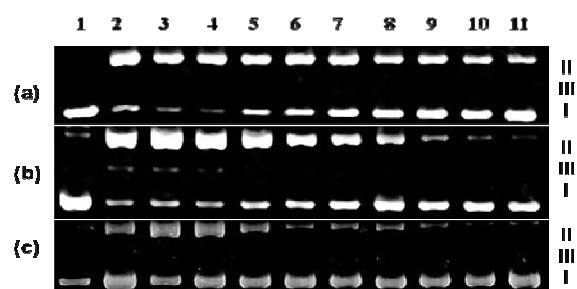
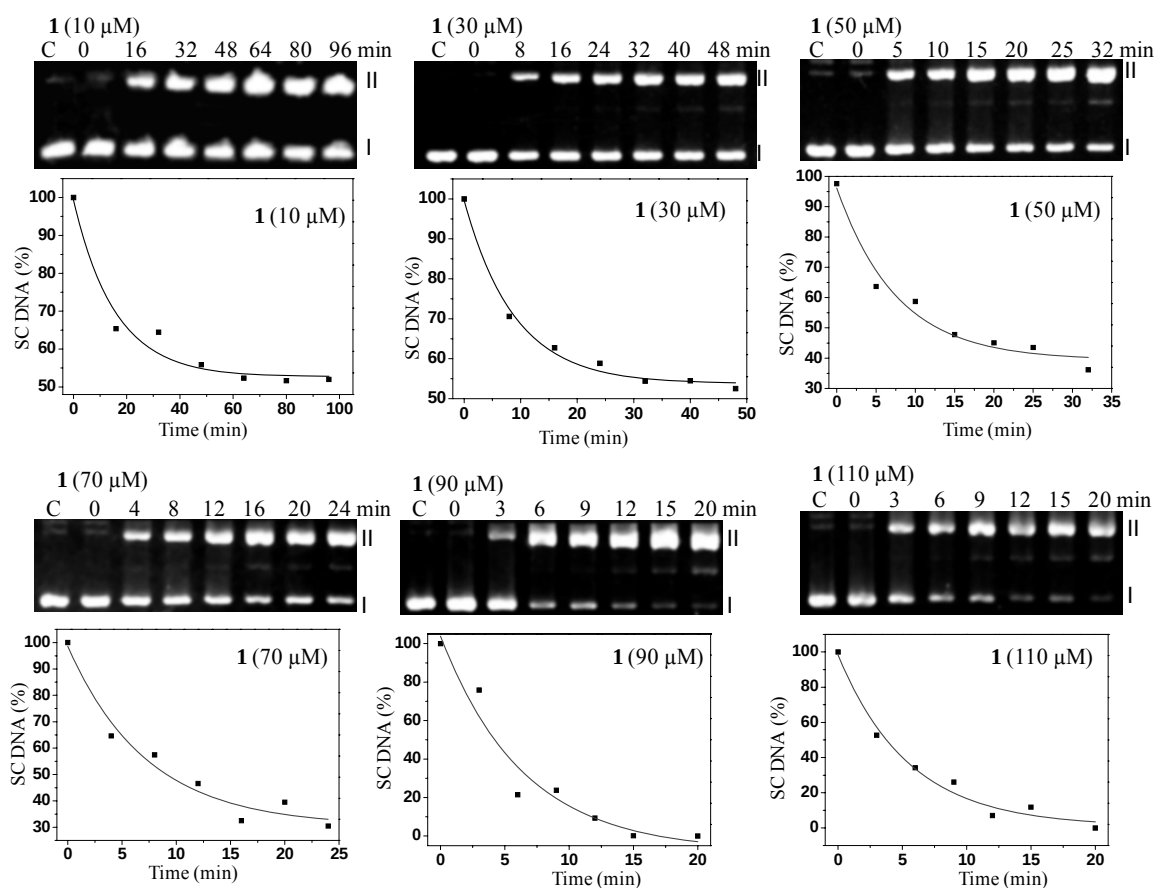


Fig. S8.



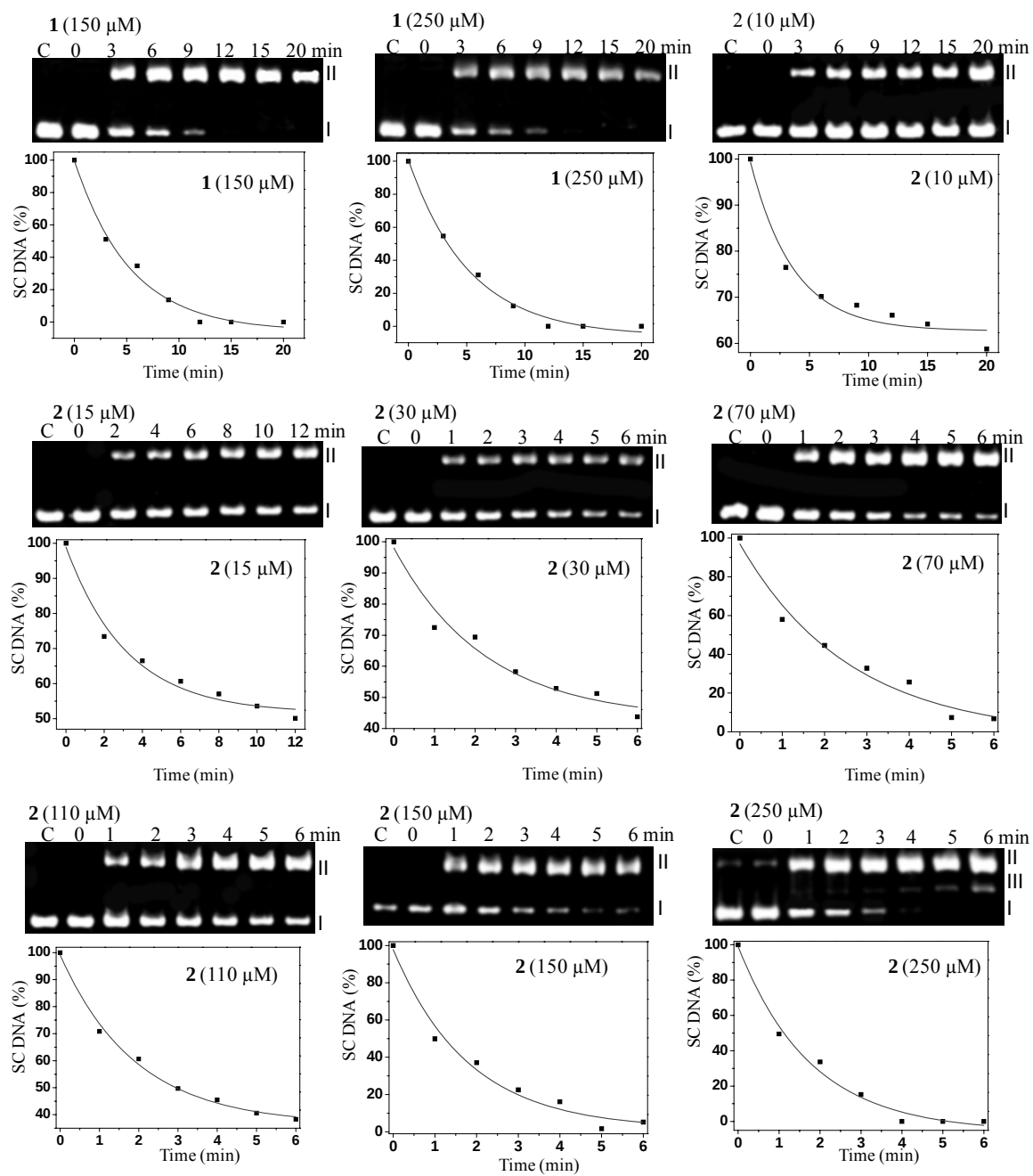


Fig. S9.

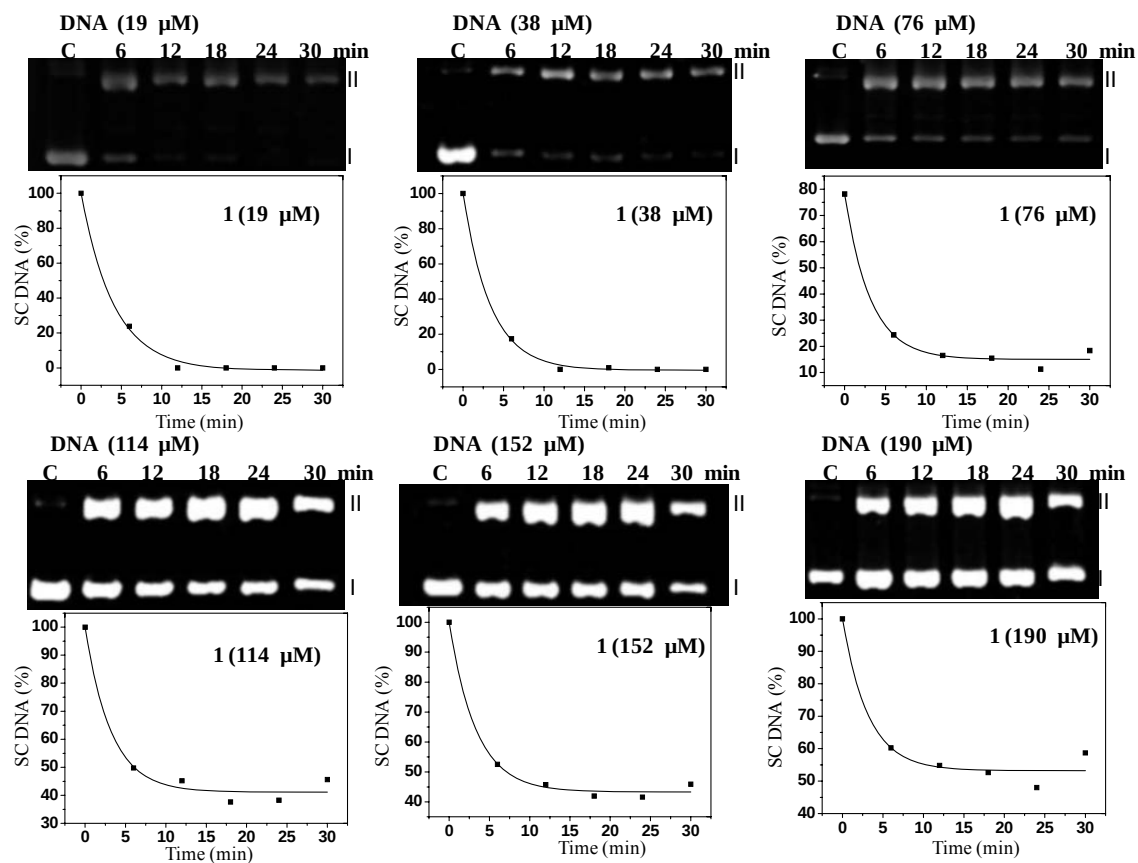


Fig. S10.

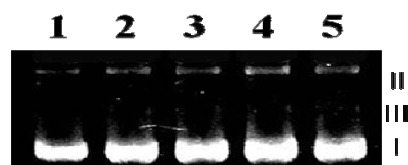


Fig. S11.

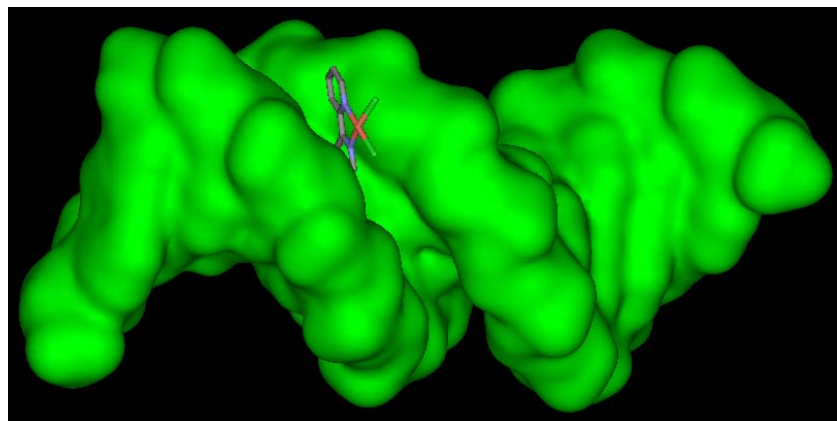


Fig. S12.