Electronic Supplementary Information for Dalton Transactions

DNA cleavage in red light promoted by copper(II) complexes of α-amino acids and photoactive phenanthroline bases

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Electronic Supplementary Information

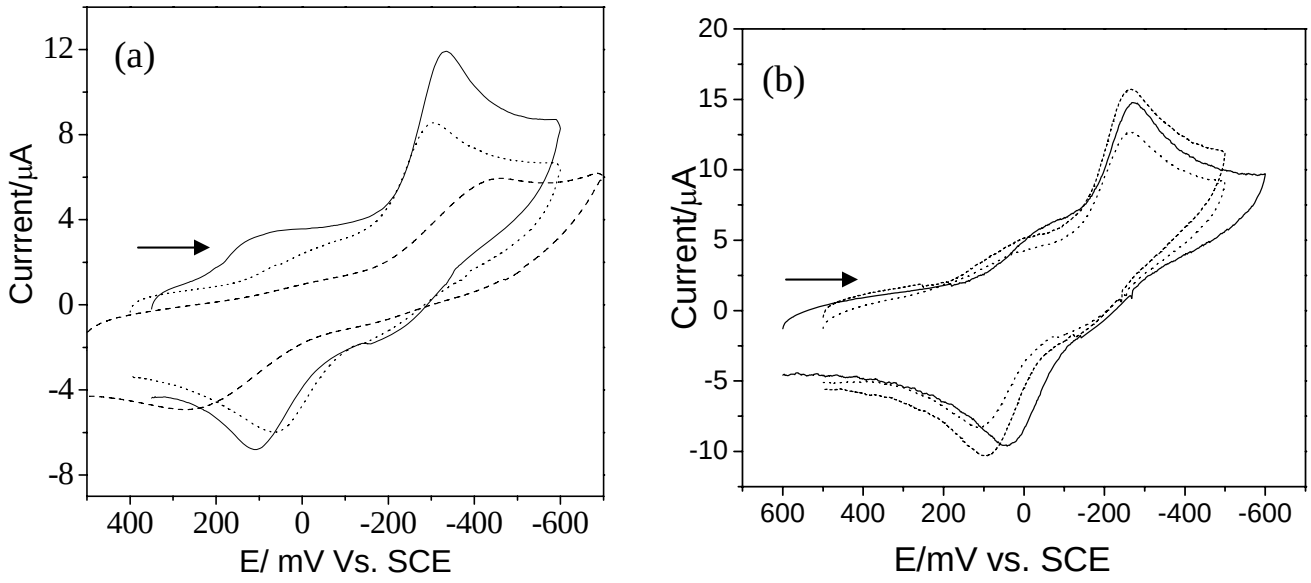

Fig. S1 Cyclic voltammograms of the complexes (a) [Cu(L-trp)(B)(H_2O)](NO_3) [**1** (—), **2** (----), **3** (……)] and (b) [Cu(L-phe)(B)(H_2O)](NO_3) [**4** (—), **5** (----), **6** (……)] in DMF-Tris buffer (1:1 v/v)-0.1 M TBAP at a scan speed of 50 mV s^{-1}.

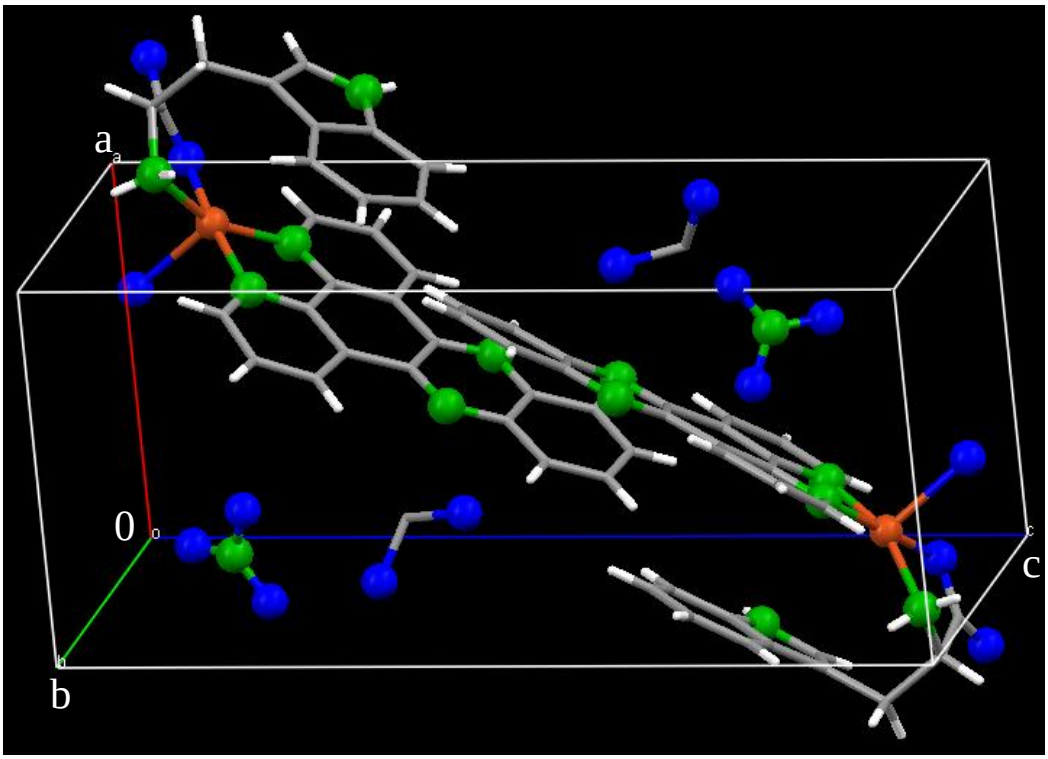

Fig. S2 Unit-cell packing diagram of [Cu(L-trp)(dppz)(H_2O)](NO_3)·MeOH (**3**·MeOH).

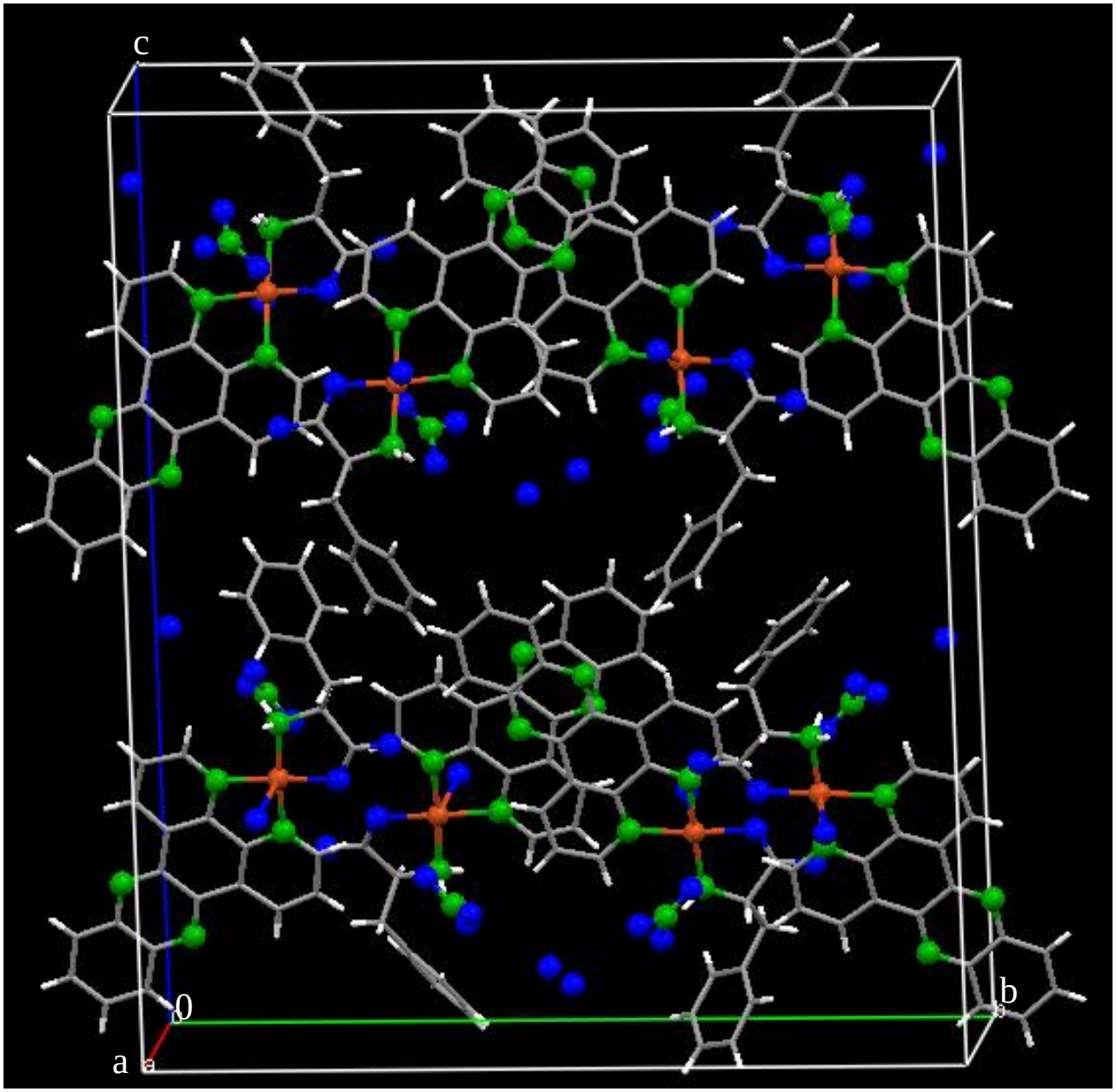

Fig. S3 Unit-cell packing diagram of[Cu(L-phe)(dppz)(H_2O)](NO_3)·H_2O (**6**·H_2O)

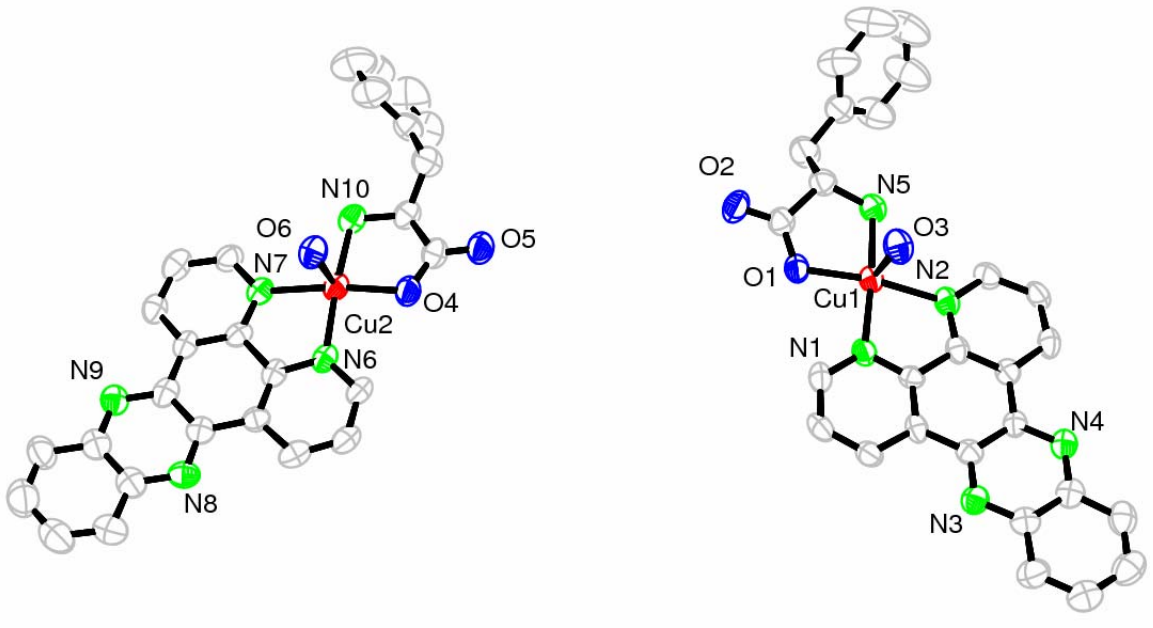

Fig. S4 ORTEP views of the two cationic complexes of [Cu(L-phe)(dppz)(H_2O)]-(NO_3)·H_2O (**6**·H_2O) showing the atom labeling scheme for the metal and hetero atoms with 50% probability thermal ellipsoids.

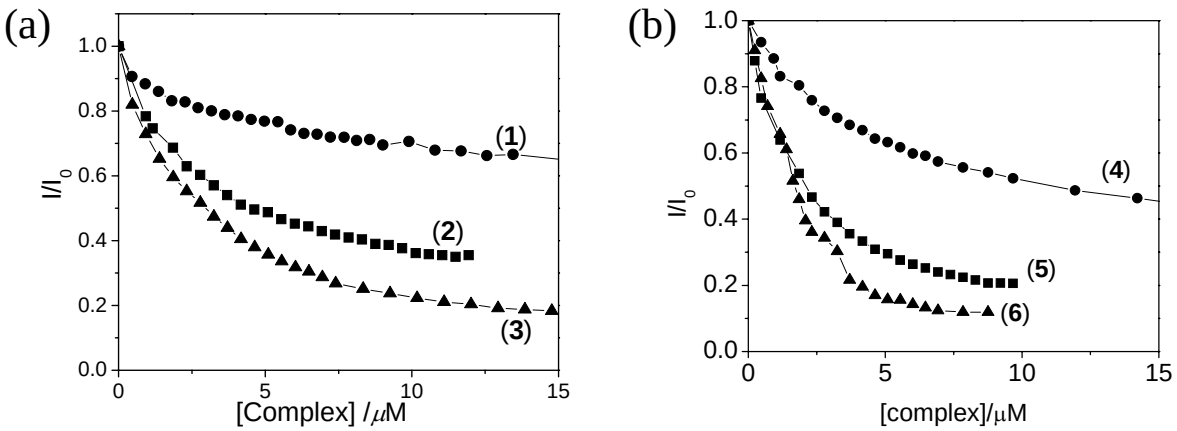

Fig. S5 Effect of addition of [Cu(L-trp)(B)(H_2O)](NO_3) (**1**-**3**) [B = phen (**1**, ●); dpq (**2**, ■); dppz (**3**, ▲) (a) and [Cu(L-phe)(B)(H_2O)](NO_3) (**4**-**6**) [B = phen (**4**, ●); dpq (**5**, ■); dppz (**6**, ▲) (b) on the emission intensity of ethidium bromide bound to CT-DNA.

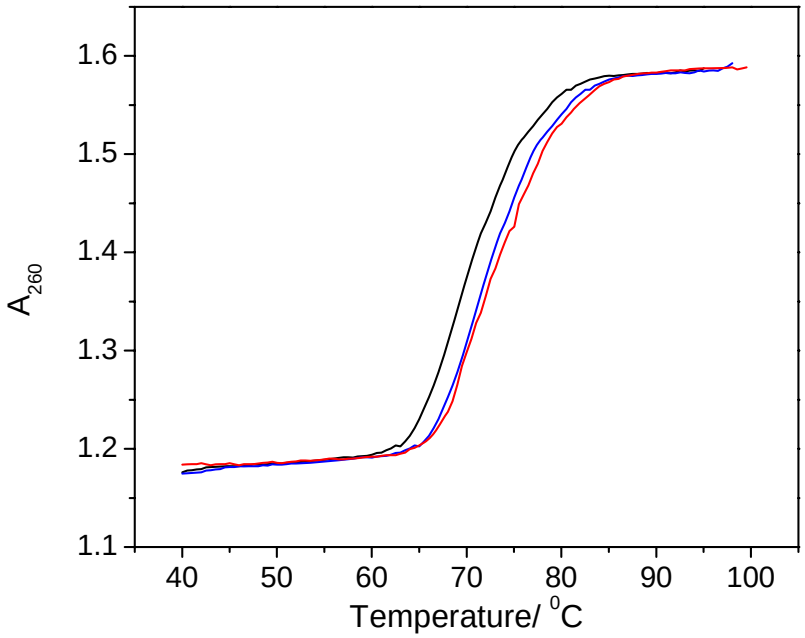

Fig. S6 DNA melting profile of CT-DNA in absence (—) and presence of complexes **5** (—) and **6** (—) in 5 mM phosphate buffer (pH, 6.85).

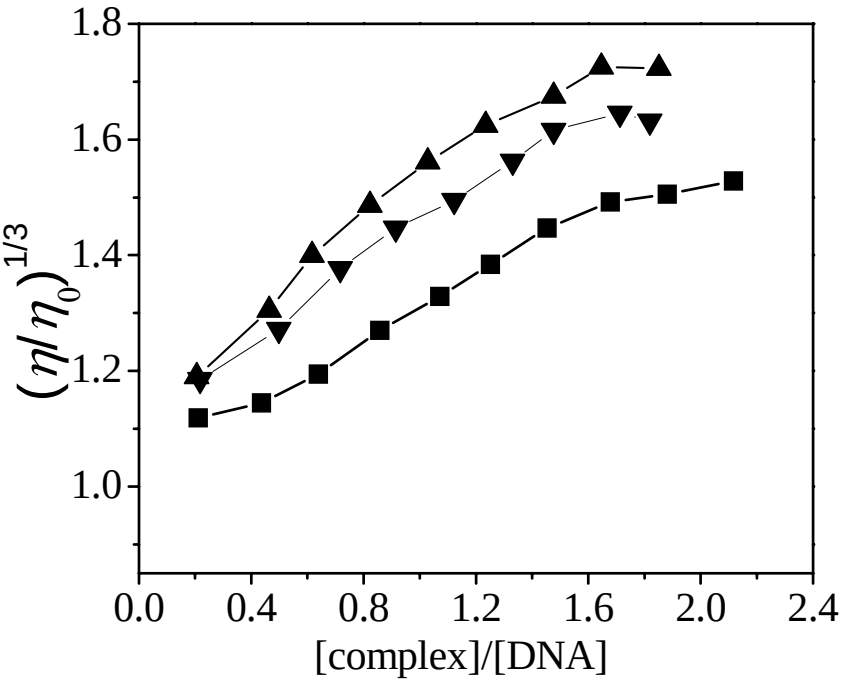

Fig. S7 Effect of increasing the amount of the complexes **4** (■), **5** (▼) and **6** (▲) on the relative viscosities of CT-DNA at 37.0 (±0.1) °C in 5 mM Tris-HCl buffer (pH, 7.2) (DNA = 160 μM).

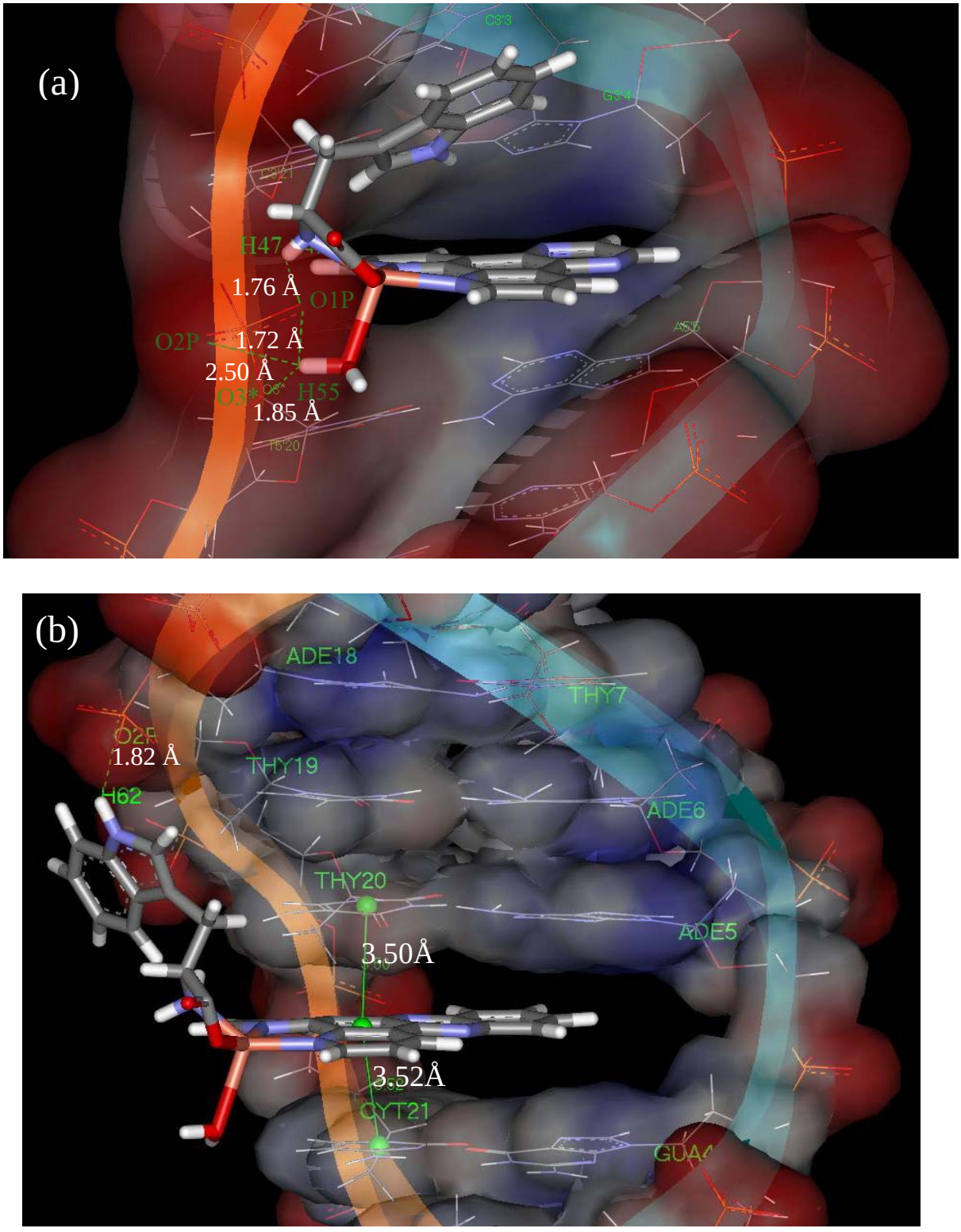

Fig. S8 (a) Stable docked state for the complex **2** showing hydrogen bonding and electrostatic interactions with d(CGCGAATTCGCG)$_2$. (b) Docked state for the complex **3** showing hydrogen bonding and stacking interactions with d(CGCGAATTCGCG)$_2$.

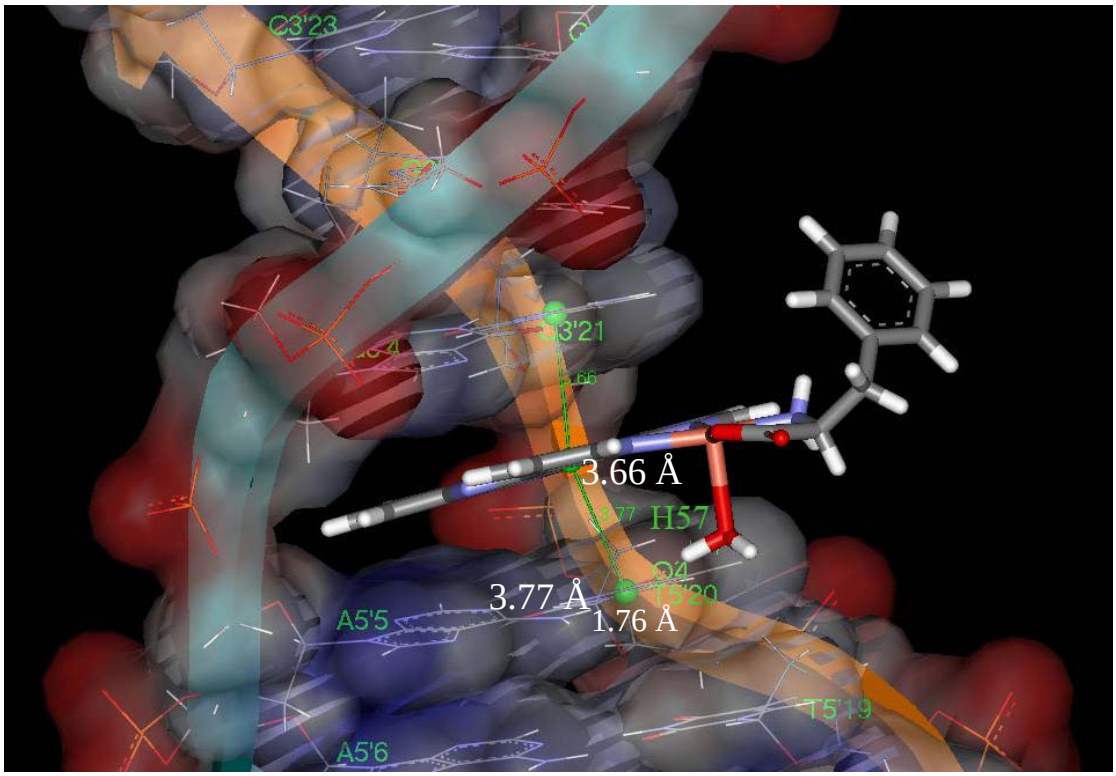

Fig. S9 Docked state for the complex **6** showing hydrogen bonding and stacking interactions with d(CGCGAATTCGCG)$_2$.

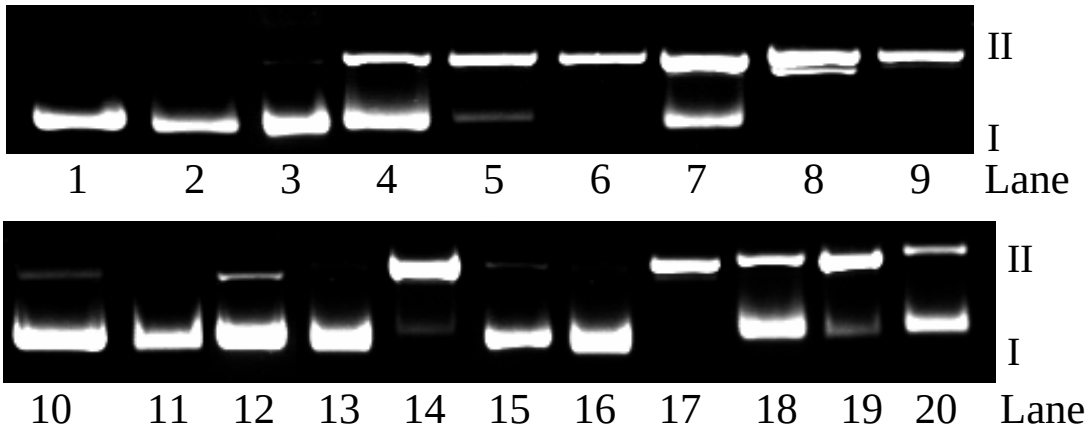

Fig. S10 Gel electrophoresis diagram showing the cleavage of SC pUC19 DNA (0.2 μg, 30 μM) by the complexes **1**-**6** (5 μM) in the presence of MPA (0.5 mM) in 50 mM Tris-HCl / NaCl buffer (pH, 7.2). Detail conditions are given below in a tabular form.

Lane No.	Reaction conditions	%NC	Lane No.		%NC
1.	DNA control	6	11.	DNA + **2** + Catalase + MPA	7
2.	DNA + MPA	8	12.	DNA+ **2** + KI + MPA	16
3.	DNA + **2** (dark)	8	13.	DNA + **2** + mannitol + MPA	10
4.	DNA + **1** + MPA	46	14.	DNA + **2** + SOD + MPA	84
5.	DNA + **2** + MPA	78	15.	DNA + distamycin-A (100 μM) + **1** + MPA	16
6.	DNA + **3** + MPA	86	16.	DNA + distamycin-A (100 μM) + **2** + MPA	14
7.	DNA + **4** + MPA	54	17.	DNA + distamycin-A (100 μM) + **3** + MPA	84
8.	DNA + **5** + MPA	87	18.	DNA + methyl green (100 μM) + **1** + MPA	41
9.	DNA + **6** + MPA	92	19	DNA + methyl green (100 μM) + **2** + MPA	80
10.	DNA + **2**+ DMSO + MPA	14	20	DNA + methyl green (100 μM) + **3** + MPA	23

Fig. S11 Cleavage of SC pUC19 DNA (0.2 μg, 30 μM) by the complexes **1**-**6** (5 μM) in 50 mM Tris-HCl/NaCl buffer (pH, 7.2) on photo-irradiation in UV-A light of 365 nm for 30 min exposure time. Detail conditions are given below in a tabular form:

Lane No.	Conditions	[Complex] / μM	%SC	%NC	%Linear
1.	DNA control	-	96	4	
2.	DNA + $Cu(NO_3)_2 \cdot 2H_2O$ (5 μM)	-	95	5	
3.	DNA + L-trp (5 μM)	-	93	7	
4.	DNA + L-phe (5 μM)	-	96	4	
5.	DNA + dpq (5 μM)	-	91	9	
6.	DNA + dppz (5 μM)	-	94	6	
7.	DNA + **2** (in dark)	5	93	7	
8.	DNA + **1**	5	43	57	
9.	DNA + **2**	5	4	60	36
10.	DNA + **3**	5	3	55	42
11.	DNA + **4**	5	94	6	
12.	DNA + **5**	5	54	46	
13.	DNA + **6**	5	62	38	
14.	DNA + Distamycin-A (100 μM) + **1**	5	90	10	
15.	DNA + Distamycin-A (100 μM) + **2**	5	86	14	
16.	DNA + Distamycin-A (100 μM) + **3**	5	6	60	34
17.	DNA + Methyl green (100 μM) + **3**	5	76	24	

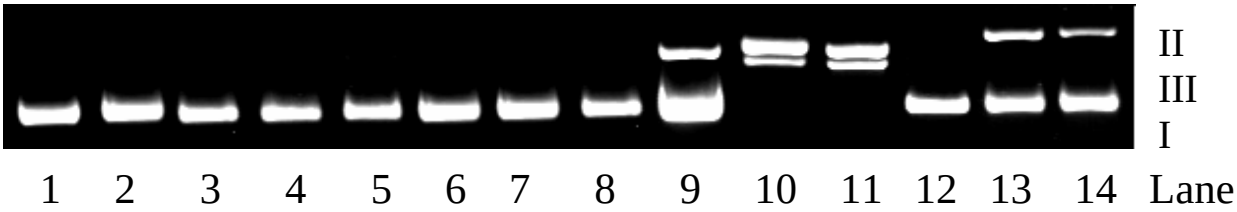

Fig. S12 Cleavage of SC pUC19 DNA (0.2 μg, 30 μM) by the complexes **1**-**6** (20 μM) in 50 mM Tris-HCl/NaCl buffer (pH, 7.2) in red light of 647.1 nm (100 mW) with an exposure time of 1 h. Detail conditions are given below in a tabular form:

Lane No.	Conditions	[Complex]/ μM	%SC	%NC	%linear
1.	DNA control	-	96	4	
2.	DNA + $Cu(NO_3)_2 \cdot 2H_2O$ (5 μM)	-	93	7	
3.	DNA + L-trp (5 μM)	-	94	6	
4.	DNA + L-phe (5 μM)	-	95	5	
5.	DNA + dpq (5 μM)	-	92	8	
6.	DNA + dppz (5 μM)	-	93	7	
7.	DNA + **3** (dark)	5	94	6	
8.	DNA + $[Cu(phen)_2]^{2+}$	5	93	7	
9.	DNA + **1**	5	64	36	
10.	DNA + **2**	5	10	65	25
11.	DNA + **3**	5	3	62	35
12.	DNA + **4**	5	92	8	
13.	DNA + **5**	5	68	32	
14.	DNA + **6**	5	76	24	

Table S1. Hydrogen bonding and π-π stacking interactions distances for the energy minimized docked poses of complexes **2**, **3** and **6** with d(CGCGAATTCGCG)$_2$[a]

[Cu(L-trp)(dpq)(H_2O)]$^+$ (2)		
Accptor group (Y-H)	**Donor group Z**	**Distance (Å)**
N45-H47 (ligand)	O1P-C3'21 (DNA-Chain B)	1.76
O51-H55 (ligand)	O1P-C3'21 (DNA-Chain B)	1.72
O51-H55 (ligand)	O3*-T5'20 (DNA-Chain B)	1.85
O51-H55 (ligand)	O2P-C3'31 (DNA-Chain B)	2.50
[Cu(L-trp)(dppz)(H_2O)]$^+$ (3)		
N56-H62 (ligand)	O2-T19 (DNA-Chain B)	1.82
H5-C21 (DNA-Chain B)	O59-axial H_2O	3.33
HN4A-C21(DNA-Chain B)	O59-axial H_2O	3.73
Centriod (T20)(DNA-chain B)- centroid (dppz) = 3.50 Å; Centriod (C21)(DNA-chain B)- centroid (dppz) = 3.52 Å.		
[Cu(L-phe)(dppz)(H_2O)]$^+$ (6)		
O56-H57 (ligand)	O4-T5'20 (DNA-Chain B)	1.76
Centriod (C3'21)(DNA-chain B)- centroid (dppz) = 3.66 Å; Centriod (T5'20)(DNA-chain B)- centroid (dppz) = 3.77 Å.		

[a]Donor group is Z and acceptor group is Y in the hydrogen bond (Y-H • • • • Z).