Electronic Supplementary Material (ESI) for RSC Advances.

Coordination versatility of phosphine derivatives of fluoroquinolones. New Cu(I) and Cu(II) complexes and their interactions with DNA.

A. Bykowska, R. Starosta, J. Jezierska and Małgorzata Jeżowska-Bojczuk

[a]*Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław,*

Table S1. Data from NMR spectra in $CDCl_3$ of compounds **PCp**, **PNr** and their copper(I) complexes.

	PCp		**[Cu^{I}-PCp]**		**PNr**		**[Cu^{I}-PNr]**	
	δ [ppm]	J[Hz]	δ [ppm]	J[Hz]	δ [ppm]	J[Hz]	δ [ppm]	J[Hz]
^{31}P	- 27.42		-18.80		- 27.50		-18.14	
H^{Ph}	7.47-7.34		7.42-7.17		7.46-7.33		7.44-7.17	
H^{1}	3.29	$^{2}J(H^{1}\text{-}P) = 2.9$	n.o		3.29	$^{2}J(H^{1}\text{-}P) = 2.8$	3.59	
H^{2,6}	3.37		3.21		3.36		3.16	
H^{3,5}	2.90		2.79		2.89		2.77	
H^{16}	7.47 - 7.34		7.42-7.17		6.82	$^{4}J(H^{16}\text{-}F) = 6.8$	6.76	$^{4}J(H^{16}\text{-}F) = 6.9$
H^{13}	7.95	$^{3}J(H^{13}\text{-}F) = 13.8$	7.94	$^{3}J(H^{13}\text{-}F) = 13.3$	7.95	$^{3}J(H^{13}\text{-}F) = 13.0$	8.00	$^{3}J(H^{13}\text{-}F) = 13.2$
H^{19}	8.71		8.66		8.63		8.62	
H^{21}	3.53		3.56		4.31		4.30	
H^{22}	1.39		1.39		1.56		1.57	
H^{22}	1.18		1.13		-		-	
H^{23}	15.01		15.06		15.13		15.14	
H$^{3,8(dmp)}$	-		7.51	$^{3}J(H^{3,8}\text{-}H^{4,7}) = 8.22$			7.52	$^{3}J(H^{3,8}\text{-}H^{4,7}) = 8.22$
H$^{4,7(dmp)}$	-		8.18	$^{3}J(H^{3,8}\text{-}H^{4,7}) = 8.24$			8.19	$^{3}J(H^{3,8}\text{-}H^{4,7}) = 8.21$
H$^{5,6(dmp)}$	-		7.74				7.76	
H$^{15,16(dmp)}$	-		2.90				2.88	

Figure S1. IR spectra of **HCp** (a) and **HNr** (b) derivatives.

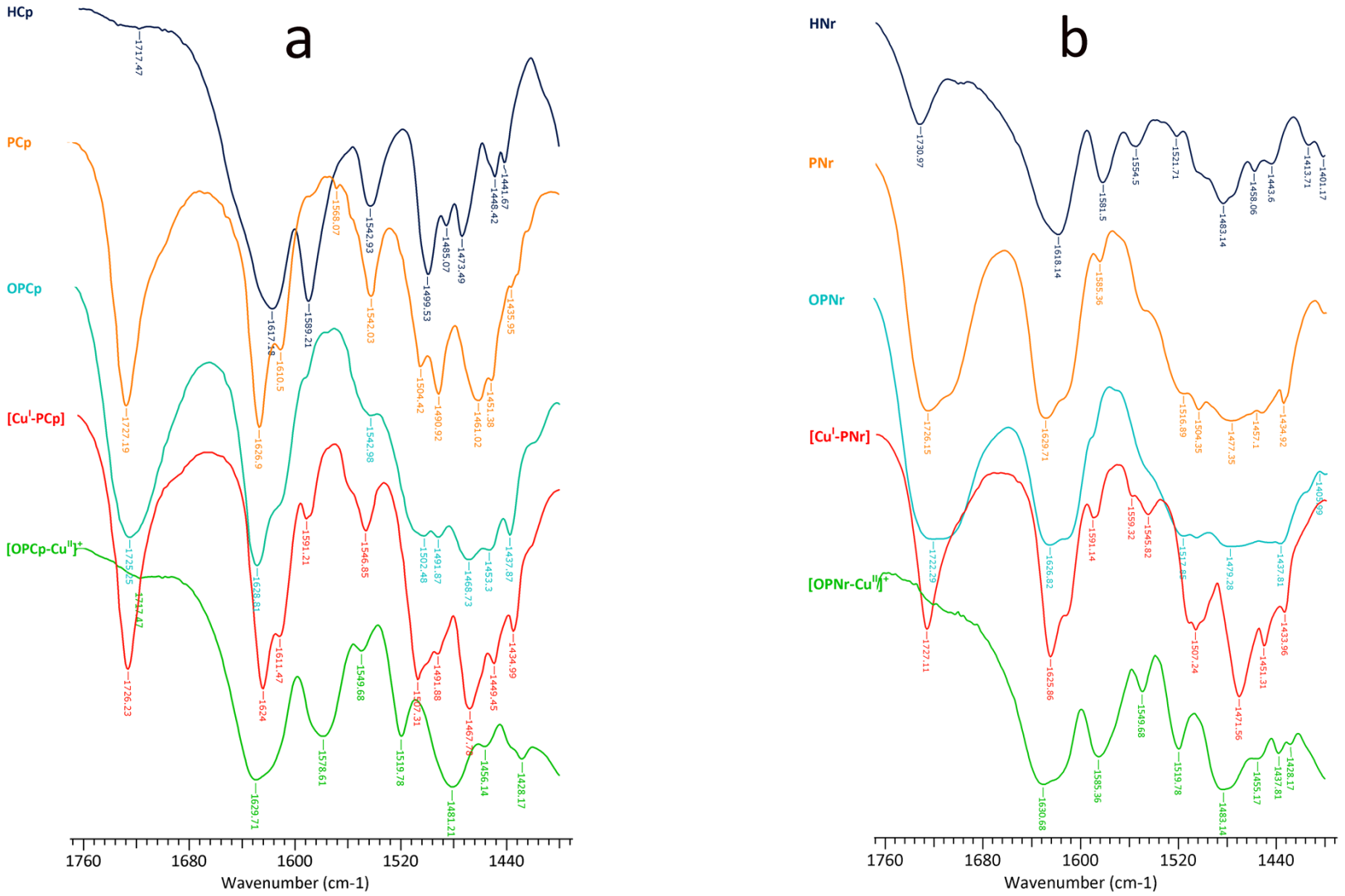


Figure S2. Electronic spectra of Cu^{I} and Cu^{II} complexes performed for the fresh solution (5 min) and after 1, 2, 4, 8, 12, 24 and 48 h.

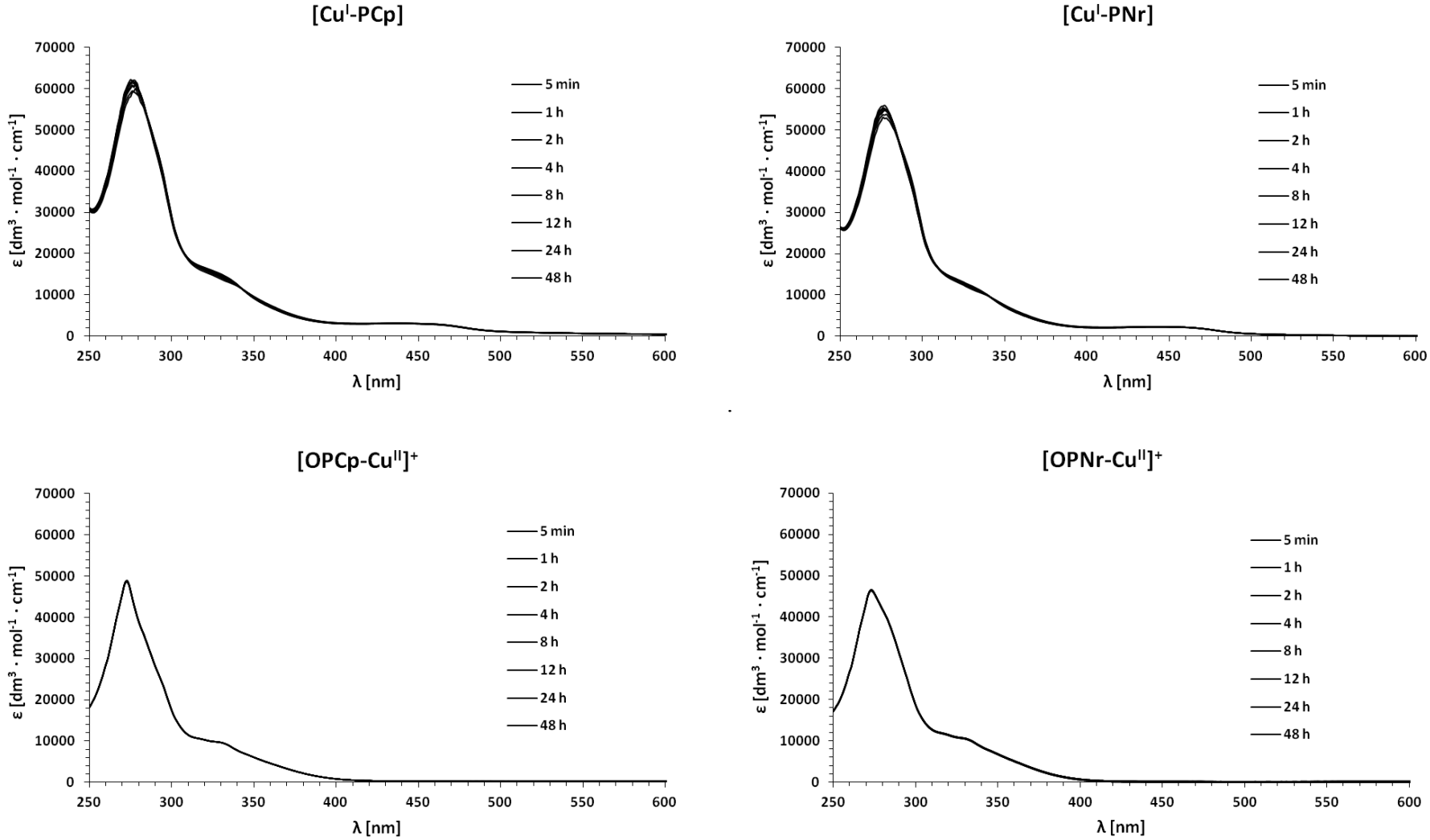
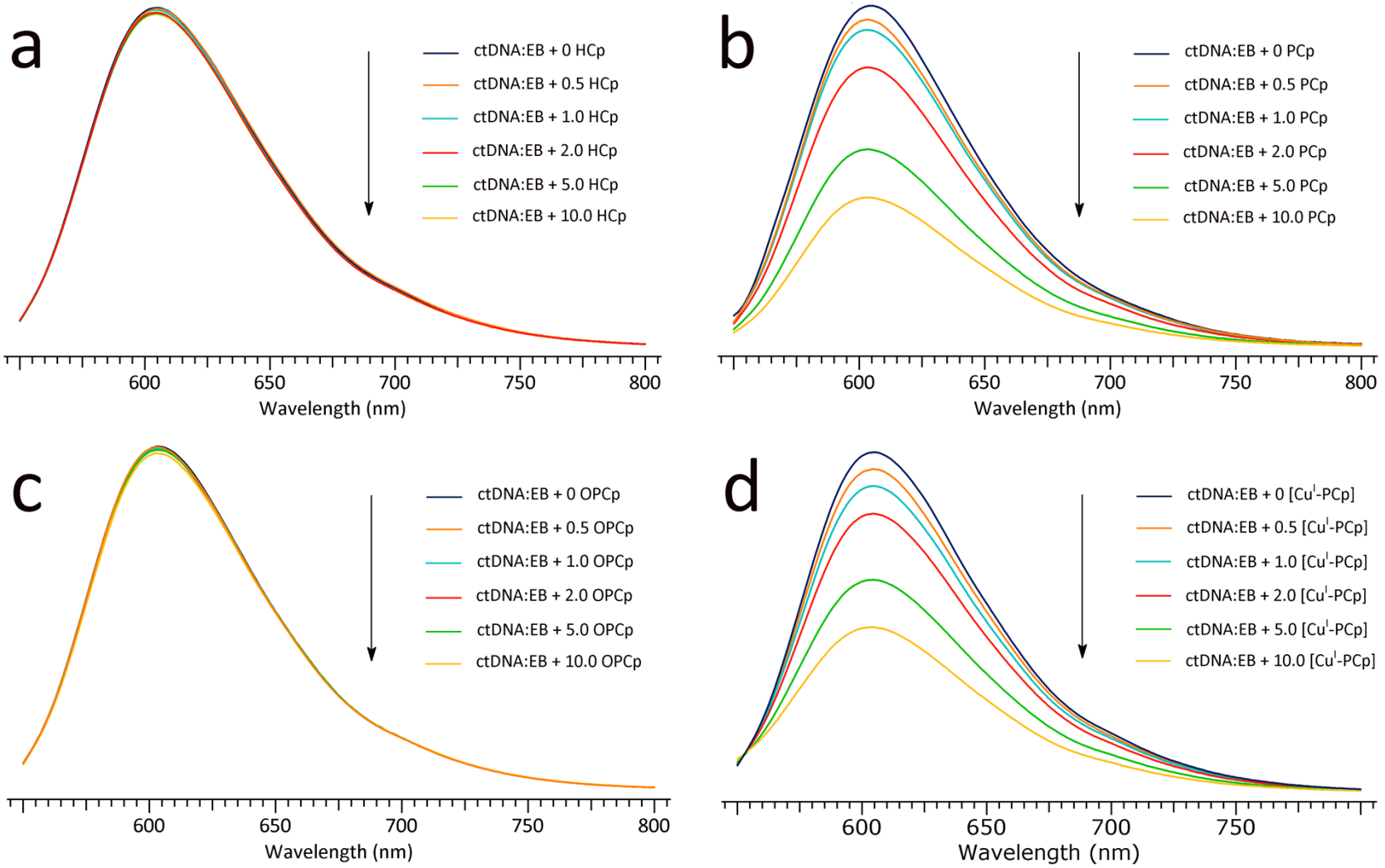


Table S2. Selected geometries of **[Cu^{I}-PCp]** and **[CuI(dmp)PPh$_3$]**. (Bond lengths [Å], angles [°])

X-ray:	[Cu^{I}-PCp]	[CuI(dmp)PPh$_3$]*
Cu1 - I1	2.5596(4)	2.6284(9)
Cu1 - N42	2.068(2)	2.090(4)
Cu1 - N41	2.130(2)	2.074(4)
Cu1 - P1	2.2184(9)	2.2052(15)
N41 - Cu1 - N42	79.98(10)	80.58(17)
I1 - Cu1 - N42	117.44(7)	117.04(12)
I1 - Cu1 - N41	118.51(7)	105.71(13)
I1 - Cu1 - P1	123.61(3)	121.26(5)
N41 - Cu1 - P1	100.56(7)	120.66(13)
N42 - Cu1 - P1	107.60(7)	117.04(12)

* R. Starosta, M. Puchalska, J. Cybińska, M. Barys and A.V. Mudring, *Dalton Trans.*, 2011, **40**, 2459-2468.

Figure S3. Fluorescence quenching of ctDNA:EB (c= $5 \cdot 10^{-5}$M) by a) **HCp**, b) **PCp**, c) **OPCp**, d) **[Cu^{I}-PCp]**, e) **[OPCp-Cu^{II}]$^{+}$**, (molar ratios 0.5; 1.0; 2.0; 5.0 and 10.0) in 50 mM pH 7.4 buffer.



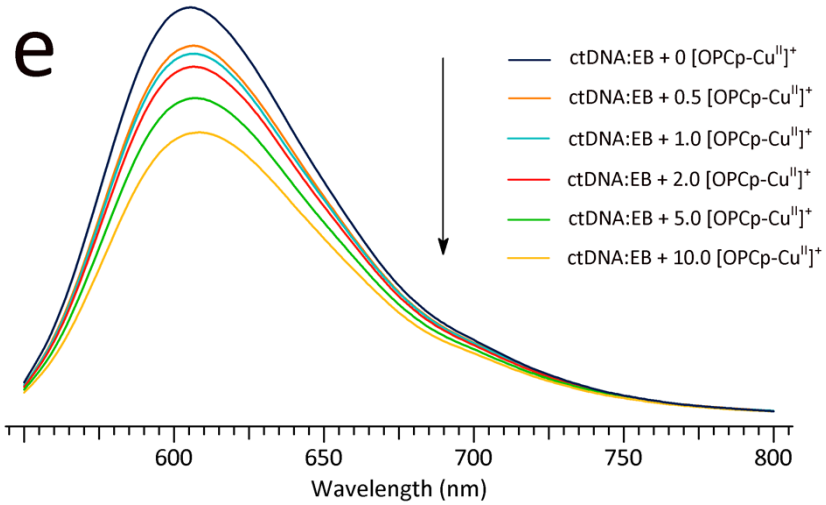
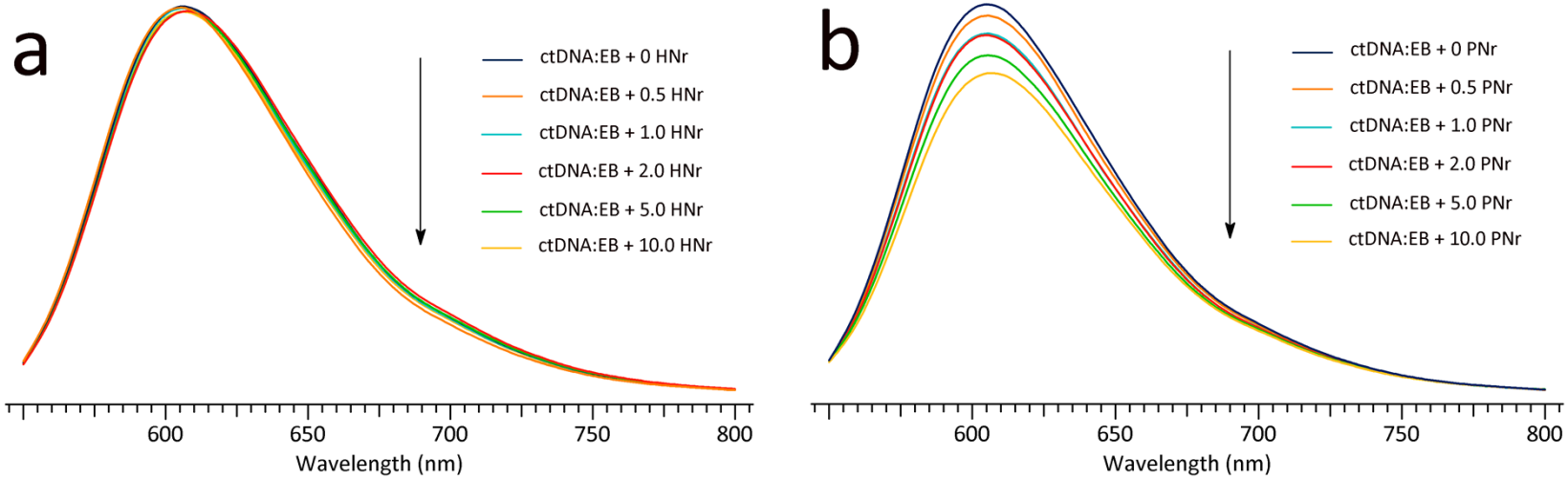


Figure S4. Fluorescence quenching of ctDNA:EB (c= $5 \cdot 10^{-5}$M) by a) **HNr**, b) **PNr**, c) **OPNr**, d) **[Cu^{I}-PNr]**, e) **[OPNr-Cu^{II}]$^{+}$**, (molar ratios 0.5; 1.0; 2.0; 5.0 and 10.0) in 50 mM pH 7.4 buffer.



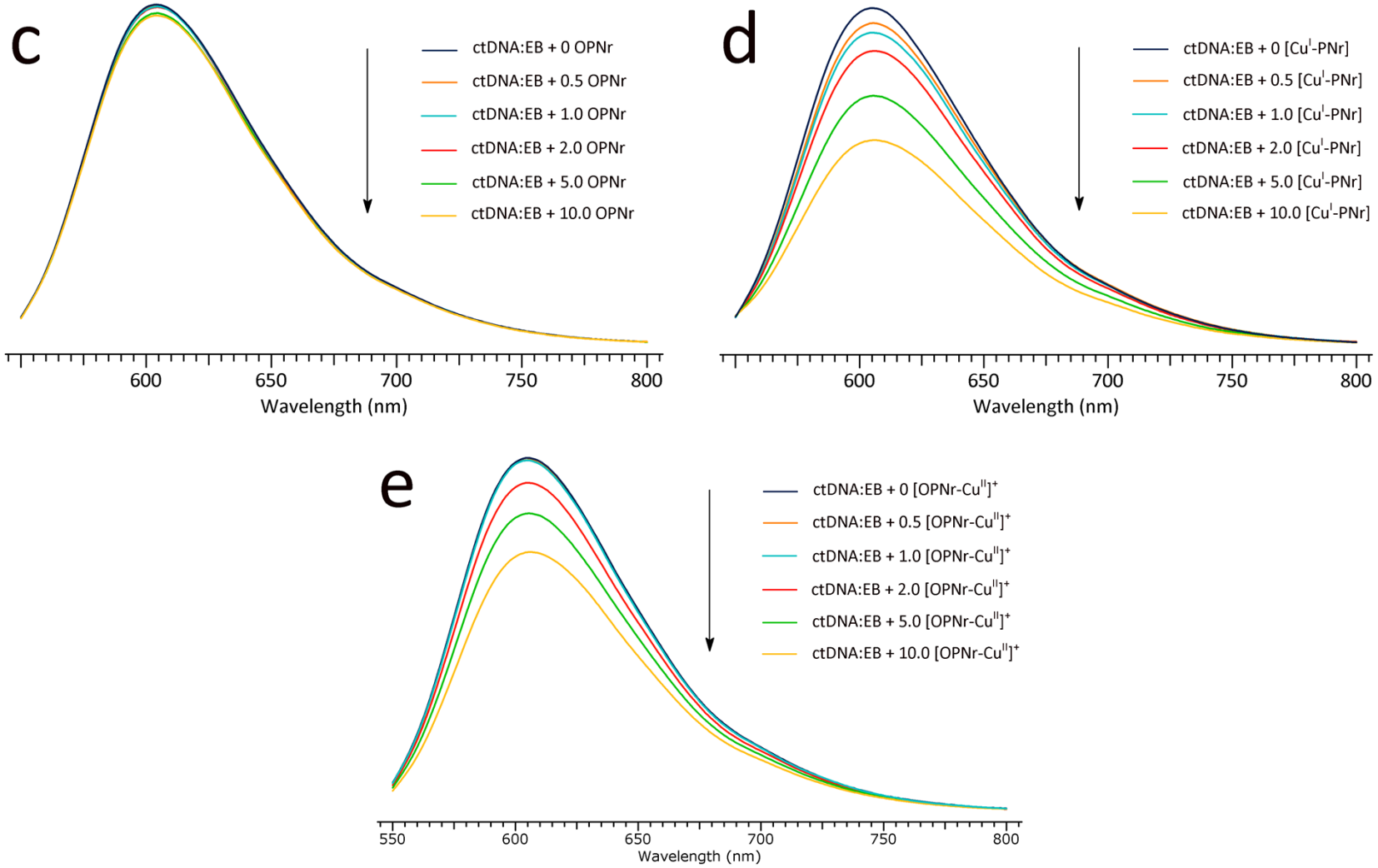

c
ctDNA:EB + 0 OPNr
ctDNA:EB + 0.5 OPNr
ctDNA:EB + 1.0 OPNr
ctDNA:EB + 2.0 OPNr
ctDNA:EB + 5.0 OPNr
ctDNA:EB + 10.0 OPNr
600
650
700
750
800
Wavelength (nm)
d
ctDNA:EB + 0 [Cu^{I}-PNr]
ctDNA:EB + 0.5 [Cu^{I}-PNr]
ctDNA:EB + 1.0 [Cu^{I}-PNr]
ctDNA:EB + 2.0 [Cu^{I}-PNr]
ctDNA:EB + 5.0 [Cu^{I}-PNr]
ctDNA:EB + 10.0 [Cu^{I}-PNr]
600
650
700
750
800
Wavelength (nm)
e
ctDNA:EB + 0 [OPNr-Cu^{II}]$^{+}$
ctDNA:EB + 0.5 [OPNr-Cu^{II}]$^{+}$
ctDNA:EB + 1.0 [OPNr-Cu^{II}]$^{+}$
ctDNA:EB + 2.0 [OPNr-Cu^{II}]$^{+}$
ctDNA:EB + 5.0 [OPNr-Cu^{II}]$^{+}$
ctDNA:EB + 10.0 [OPNr-Cu^{II}]$^{+}$
550
600
650
700
750
800
Wavelength (nm)

Figure S5. Molecular docking: preparation of the gaps.

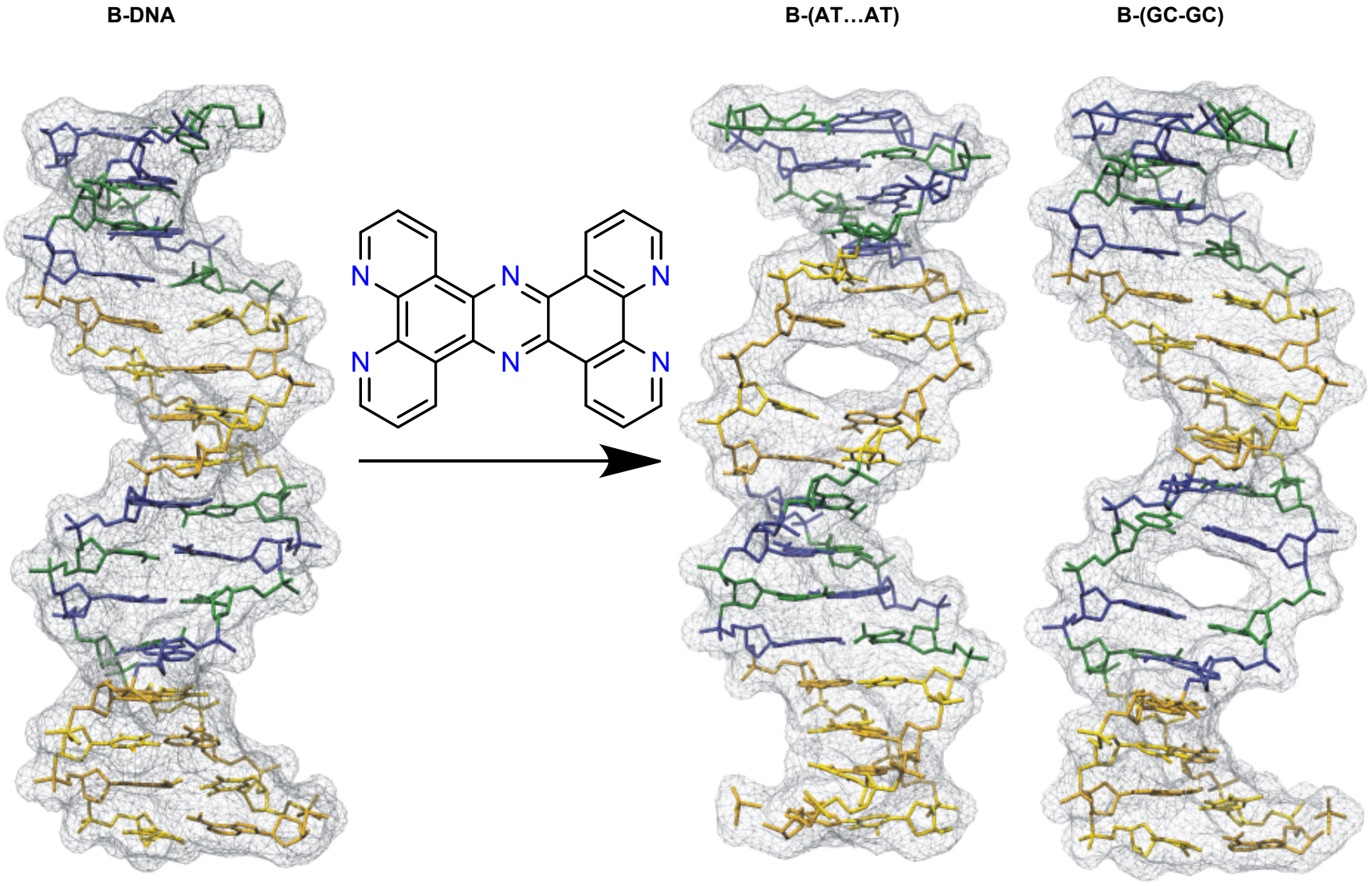
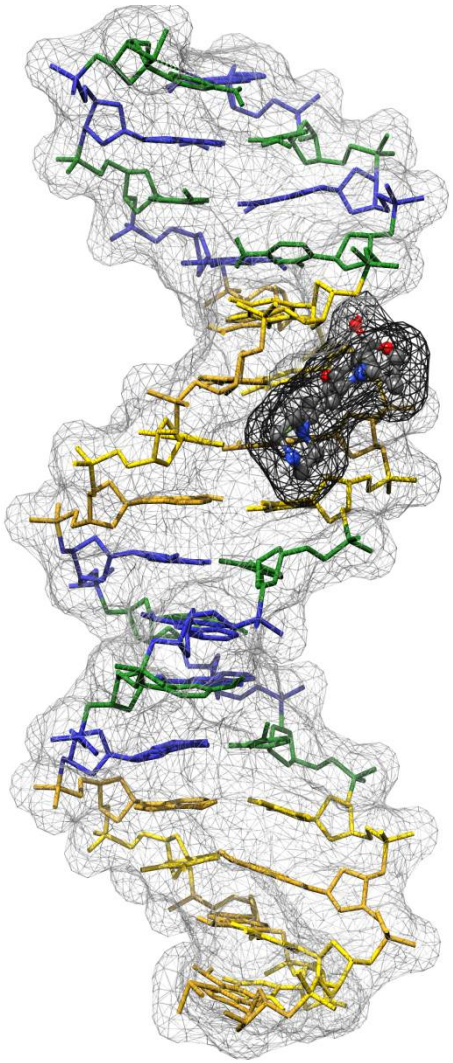
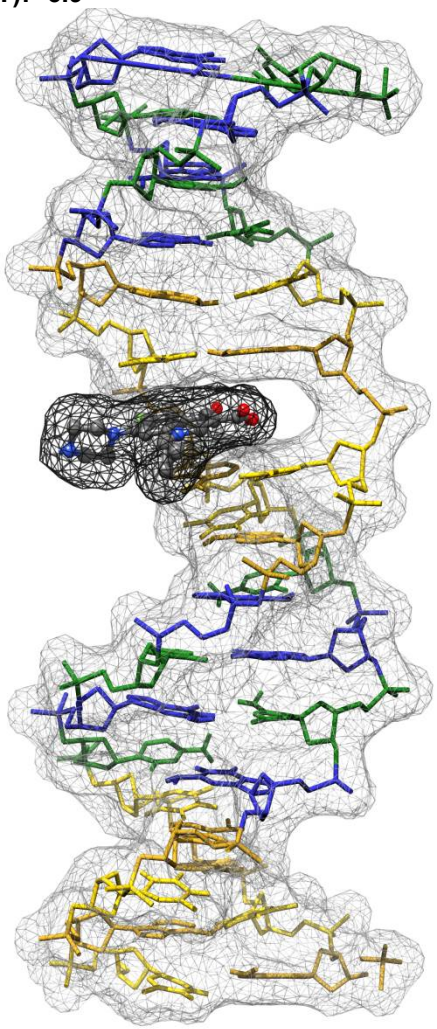


Figure S6. Molecular docking: the docking of **HCp** (with the scoring function result)

B-DNA: -7.1



B-(AT...AT): -6.9



B-(GC-GC): -7.4

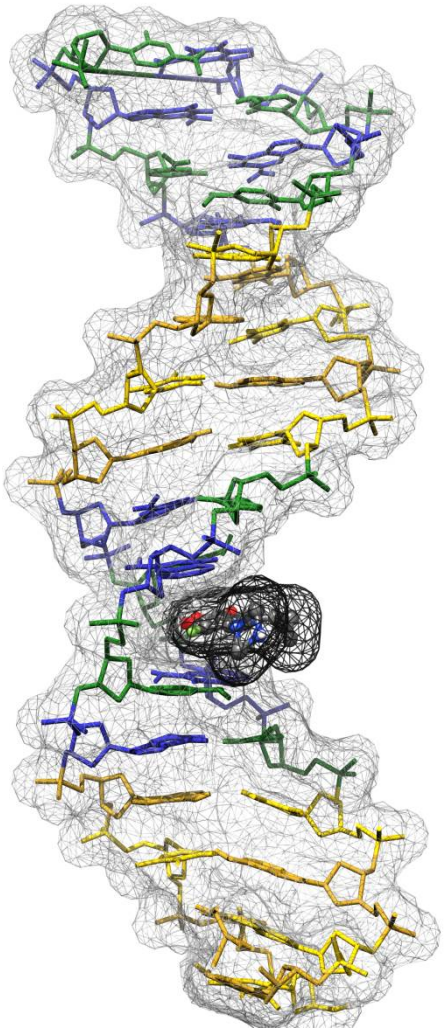


Figure S7. Molecular docking: the docking of **PCp** (with the scoring function result)

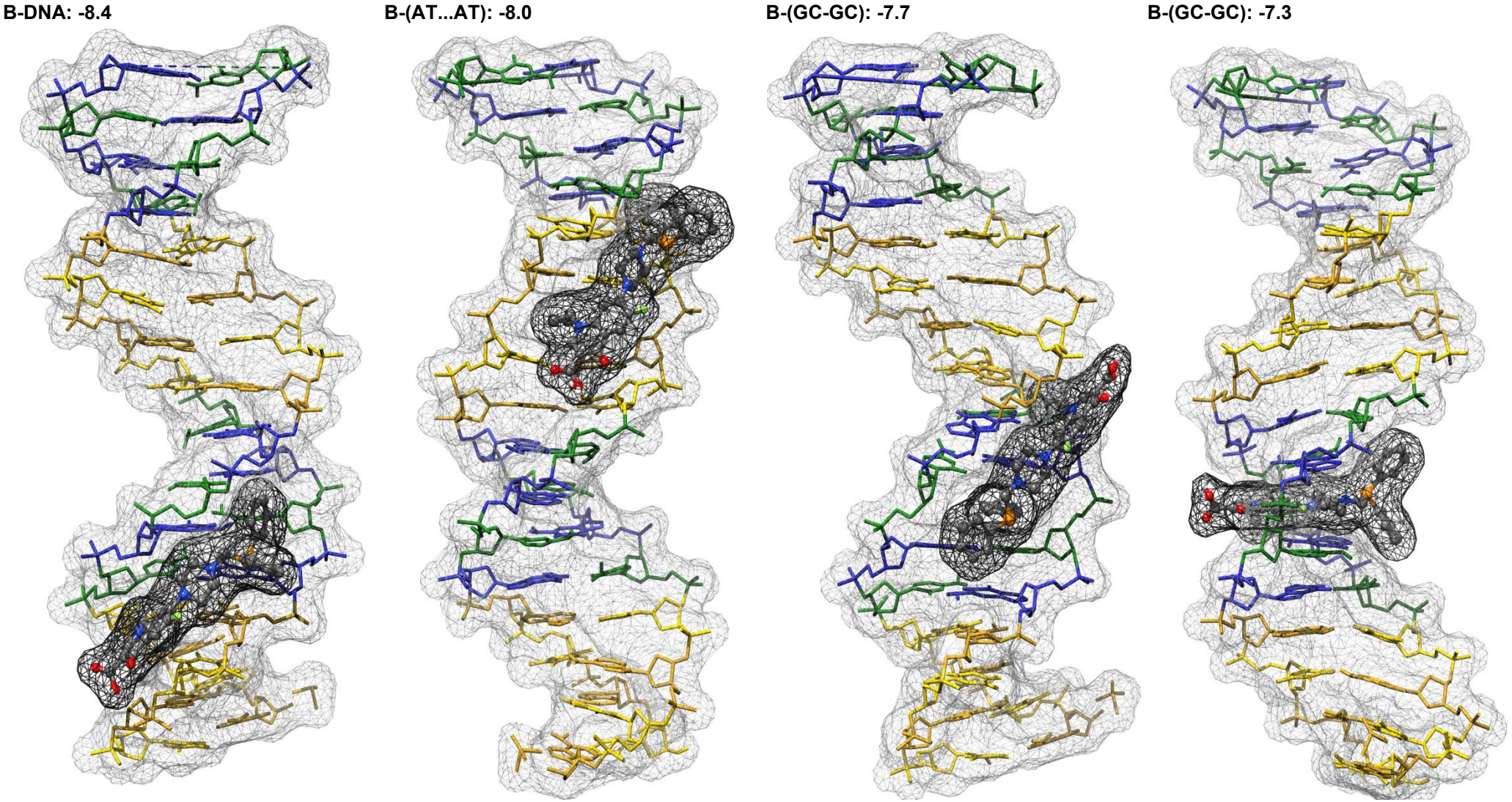
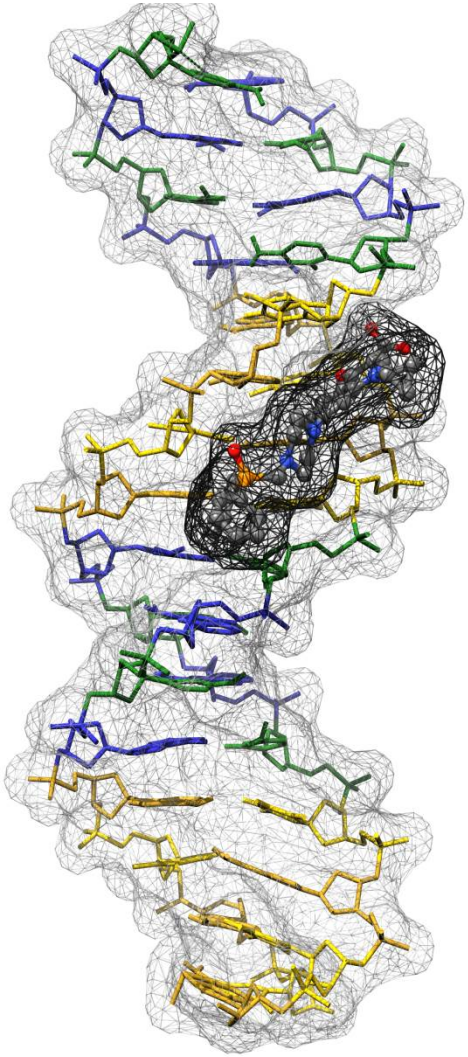
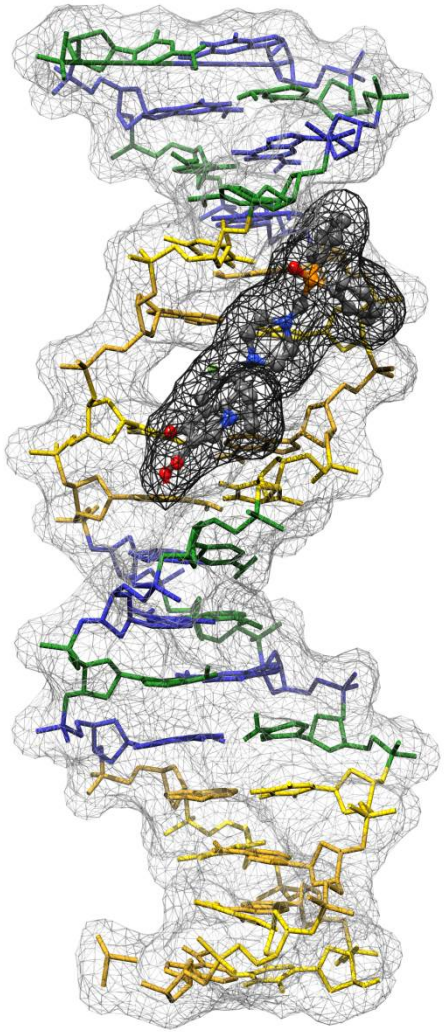


Figure S8. Molecular docking: the docking of **OPCp** (with the scoring function result)

B-DNA: -8.6



B-(AT...AT): -7.7



B-(GC-GC): -8.1

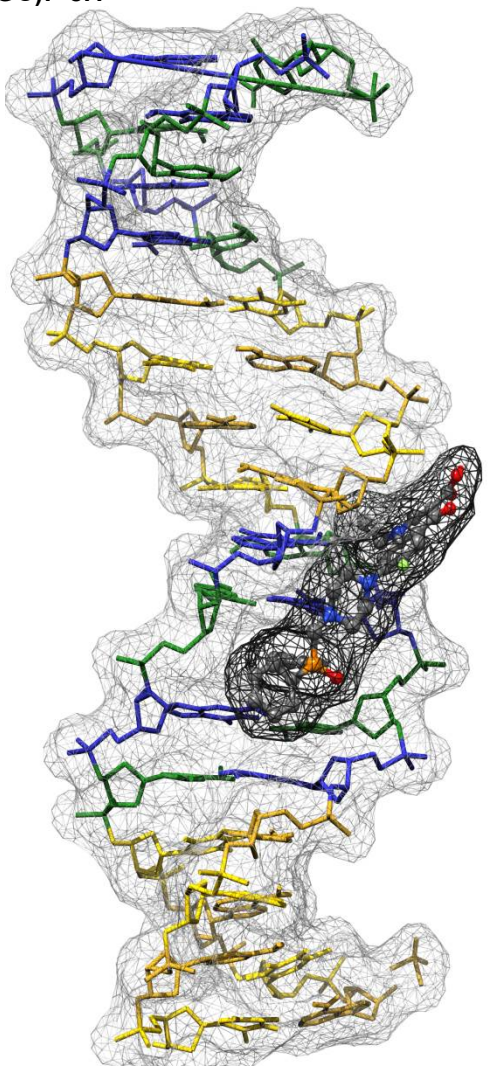


Figure S9. Molecular docking: the docking of **[Cu^{I}-PCp]** (with the scoring function result)

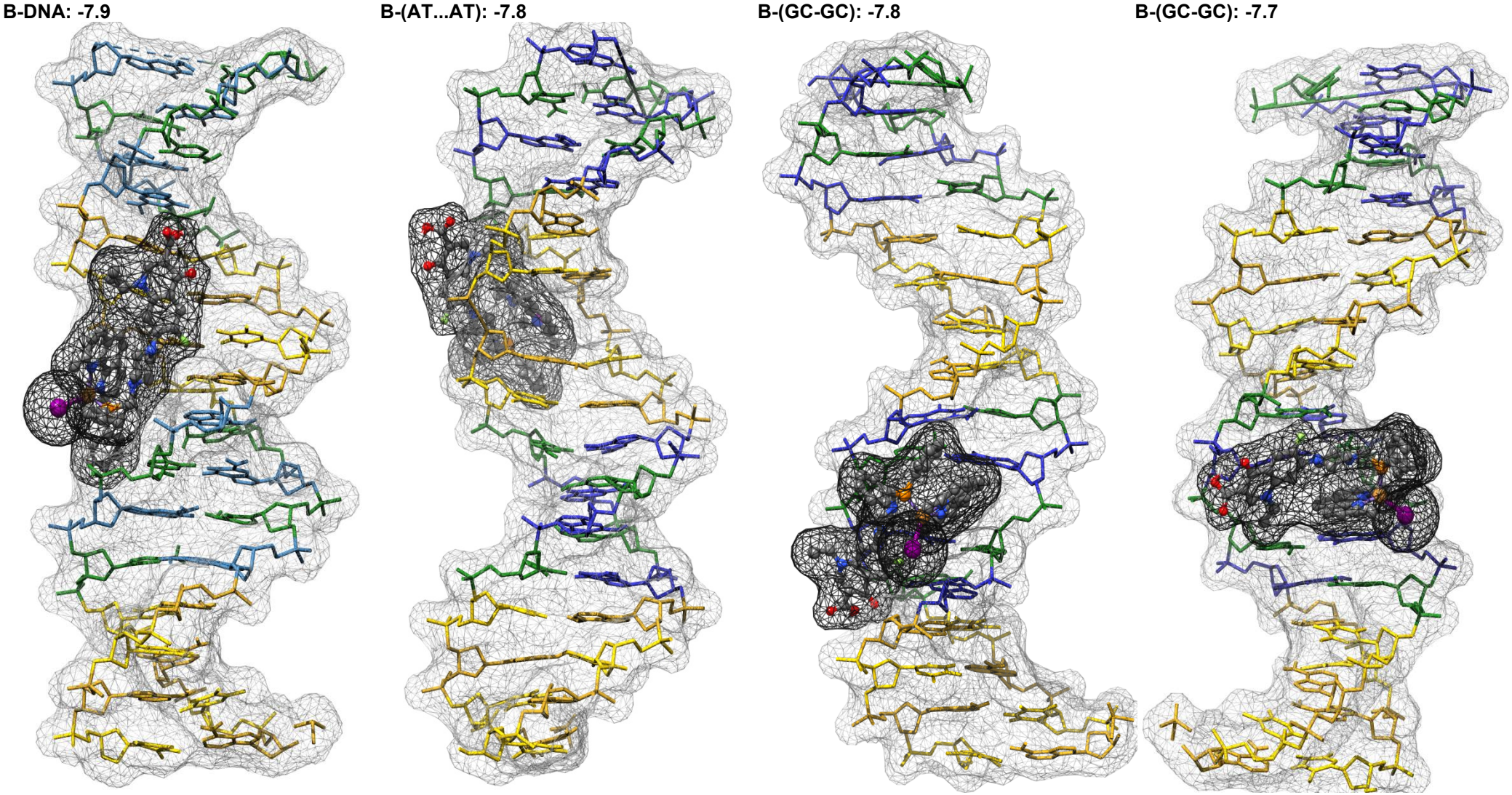
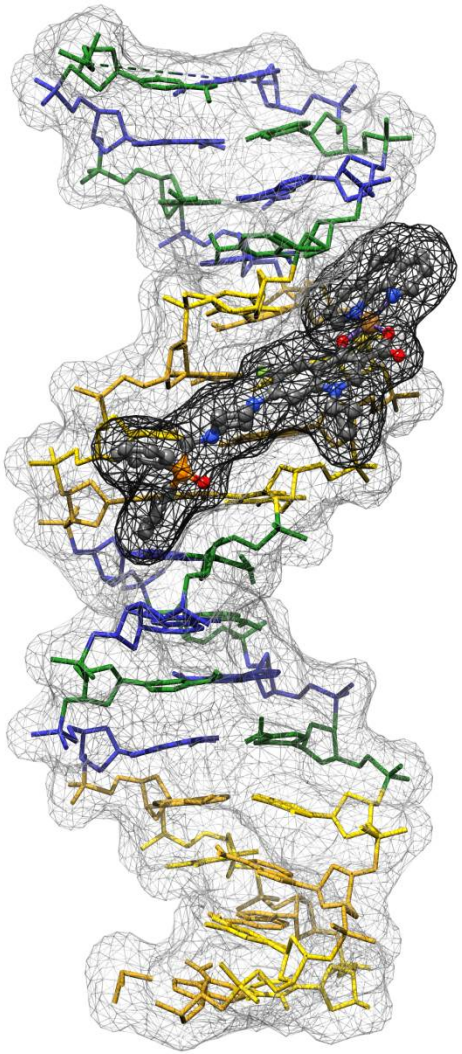
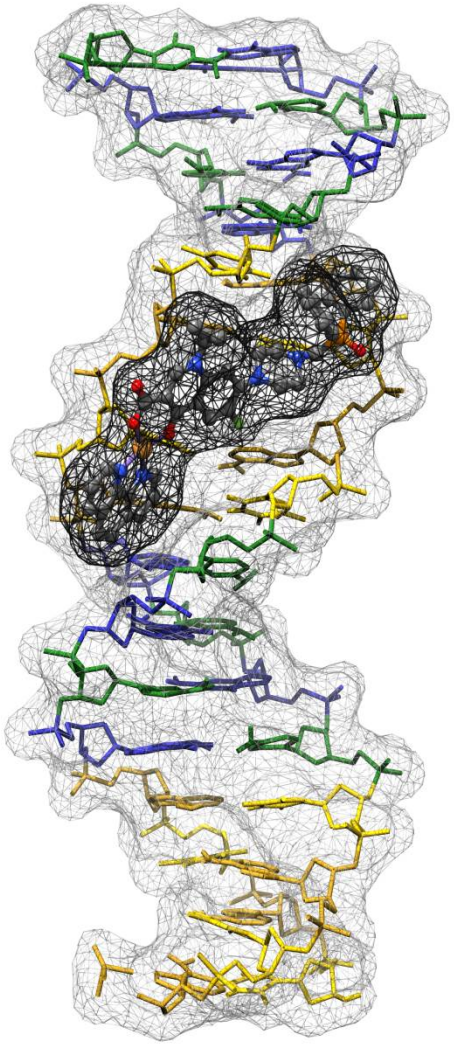


Figure S10. Molecular docking: the docking of **[OPCp-Cu^{II}]$^{+}$** (with the scoring function result)

B-DNA: -10.9



B-(AT...AT): -9.7



B-(GC-GC): -9.5

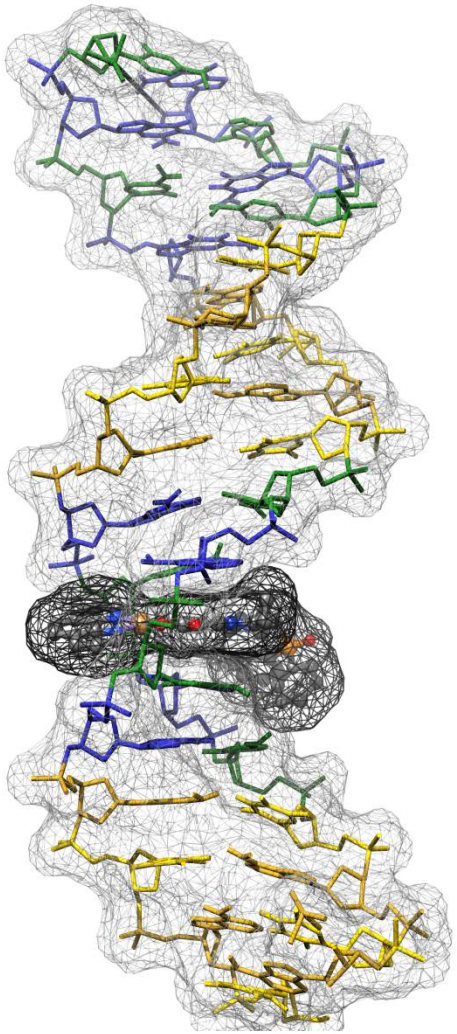


Figure S11. Molecular docking: the docking of **HNr** (with the scoring function result)

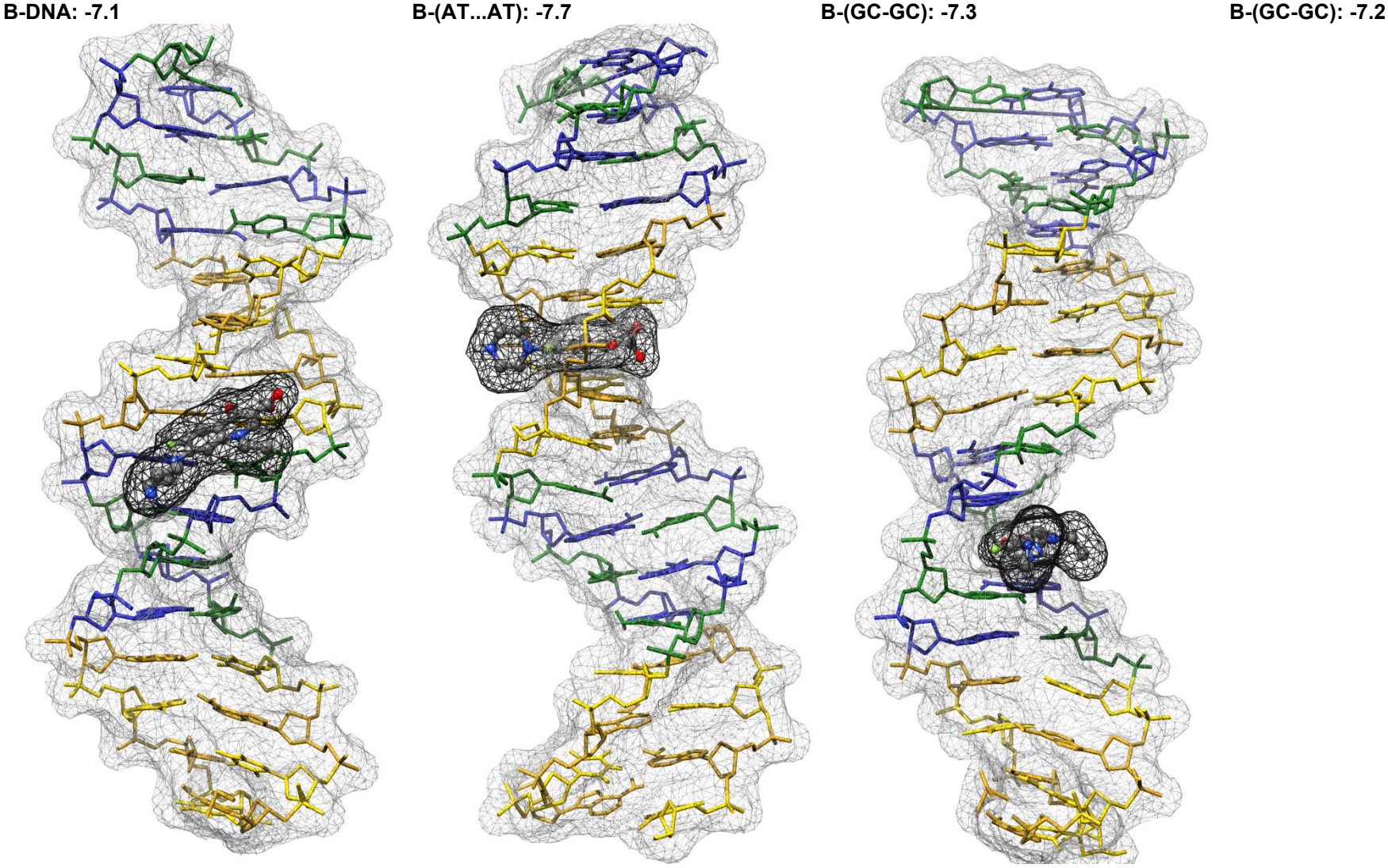
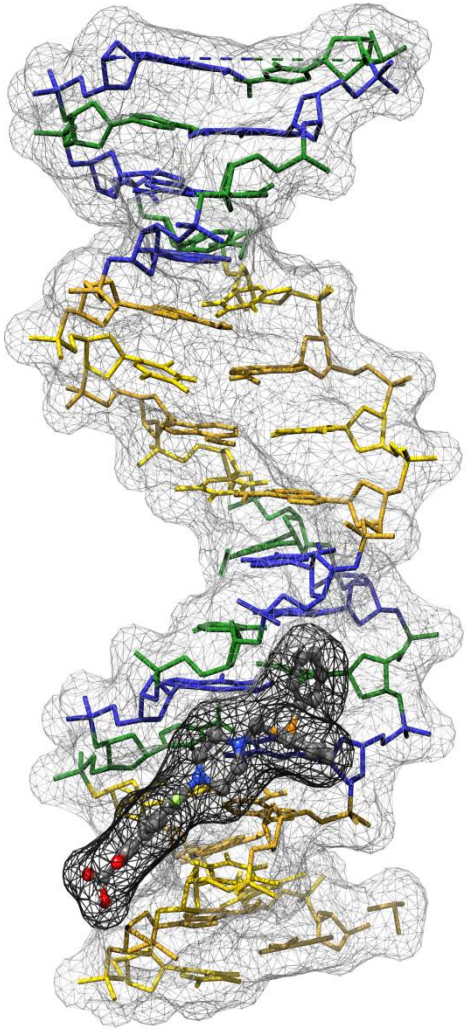
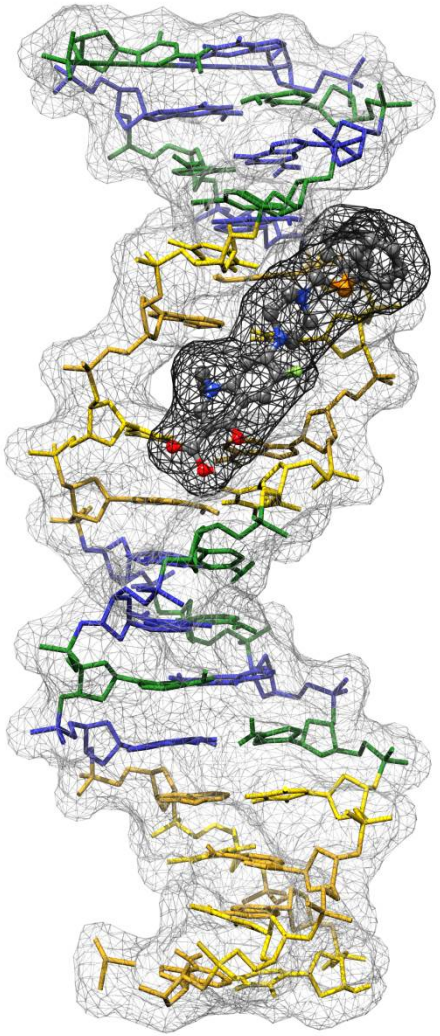


Figure S12. Molecular docking: the docking of **PNr** (with the scoring function result)

B-DNA: -8.4



B-(AT...AT): -7.9



B-(GC-GC): -8.0

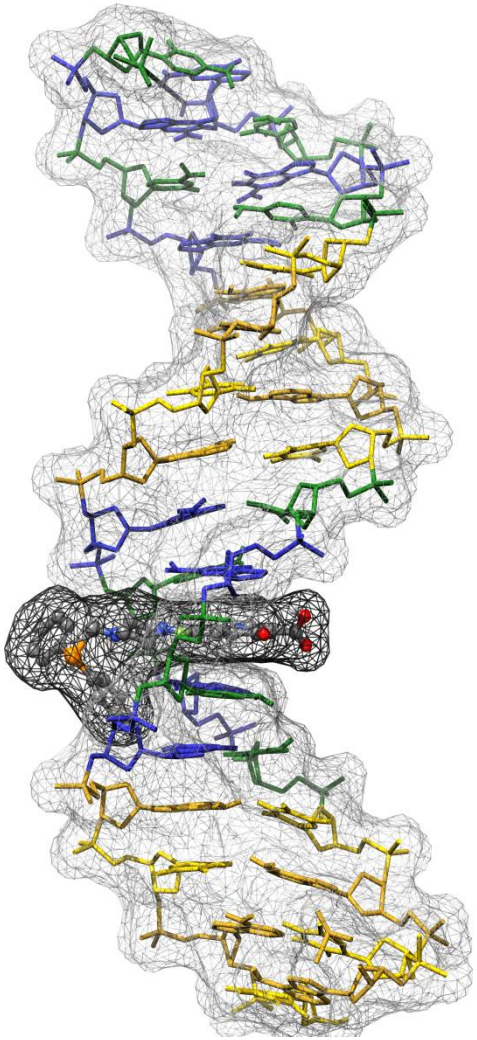


Figure S13. Molecular docking: the docking of **OPNr** (with the scoring function result)

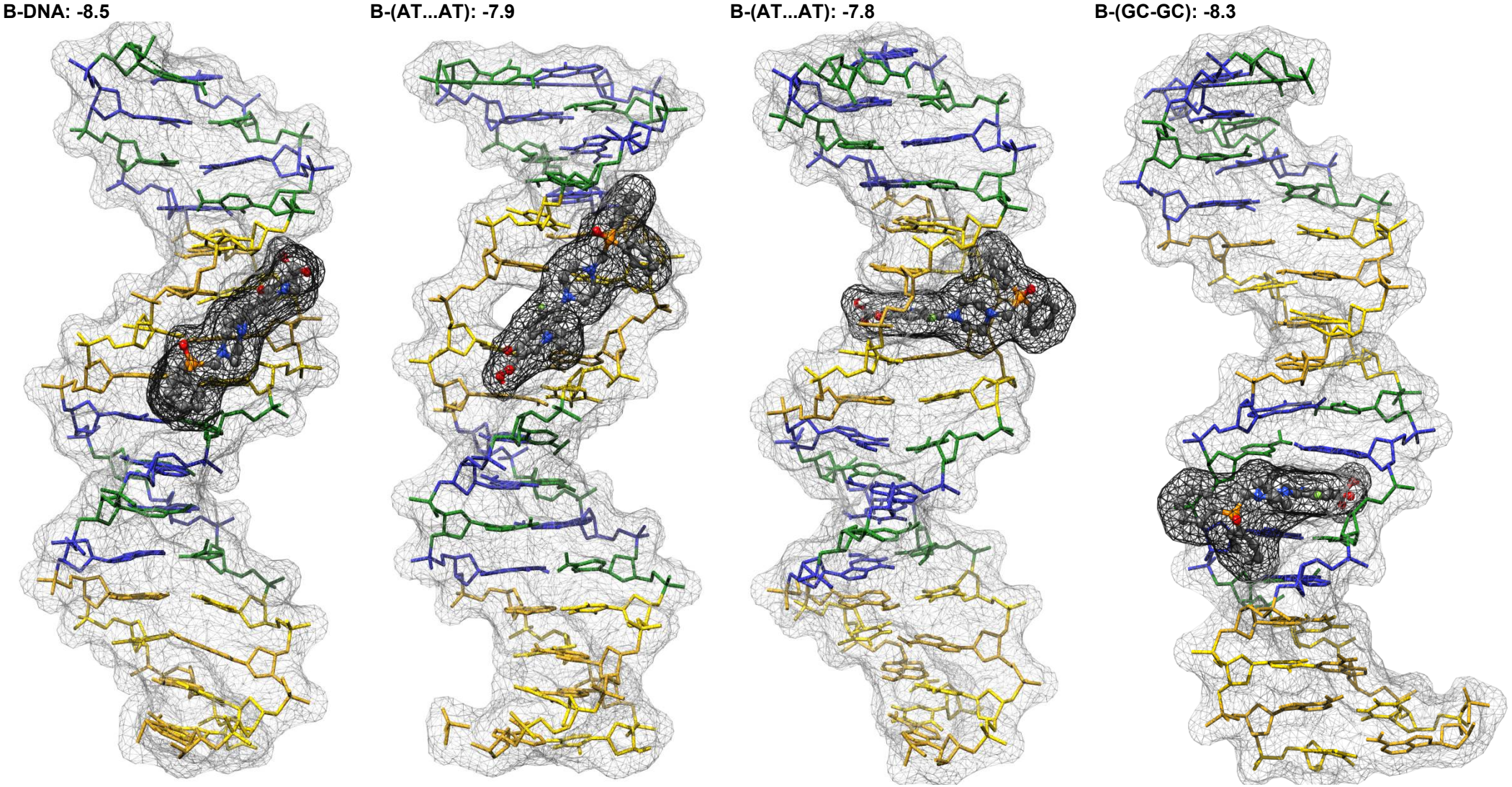
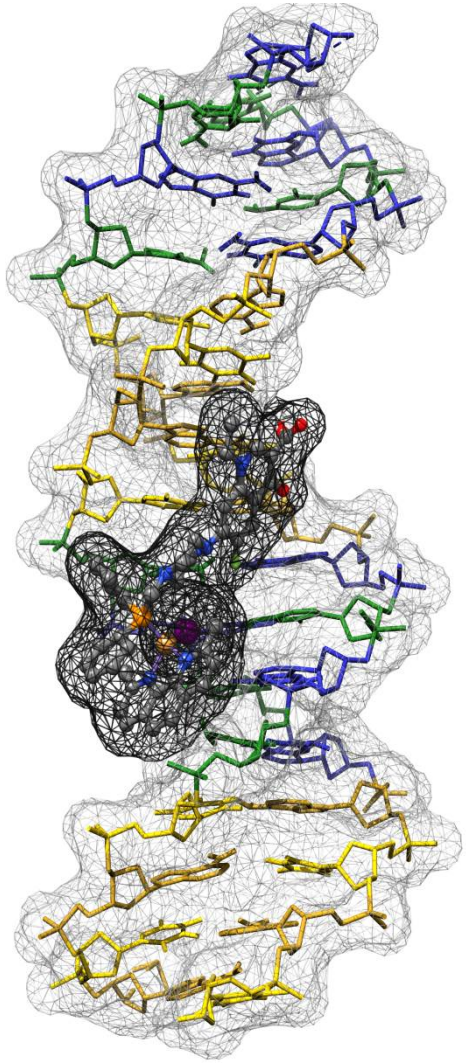
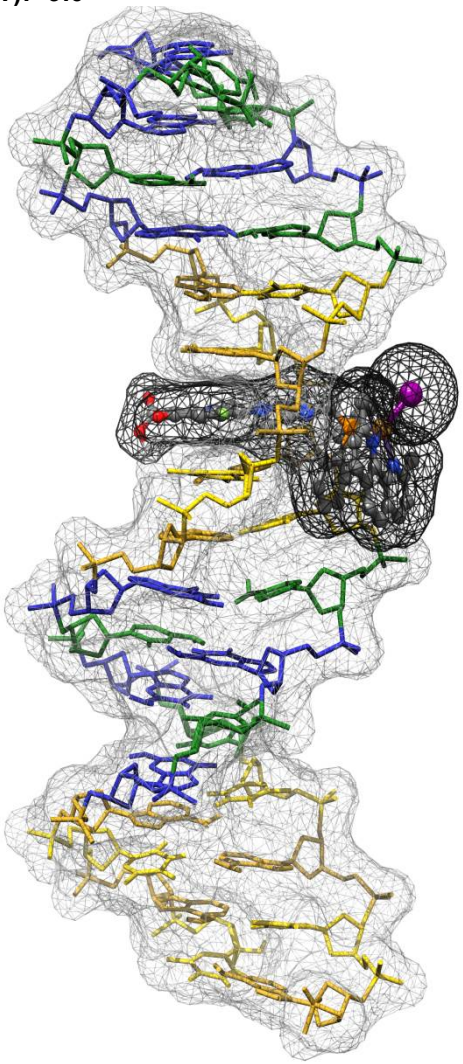


Figure S14. Molecular docking: the docking of **[Cu^{I}-PNr]** (with the scoring function result)

B-DNA: -8.1



B-(AT...AT): -9.0



B-(GC-GC): -9.1

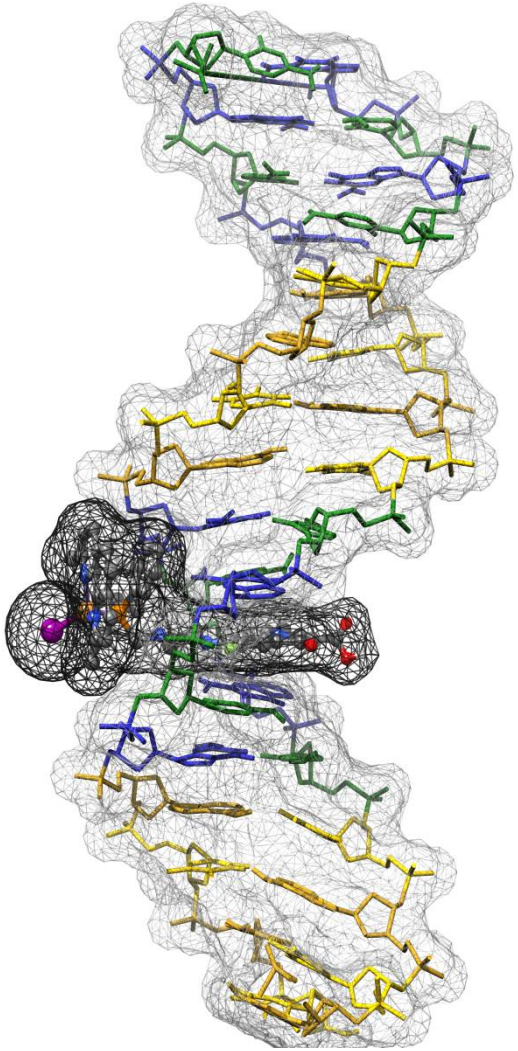
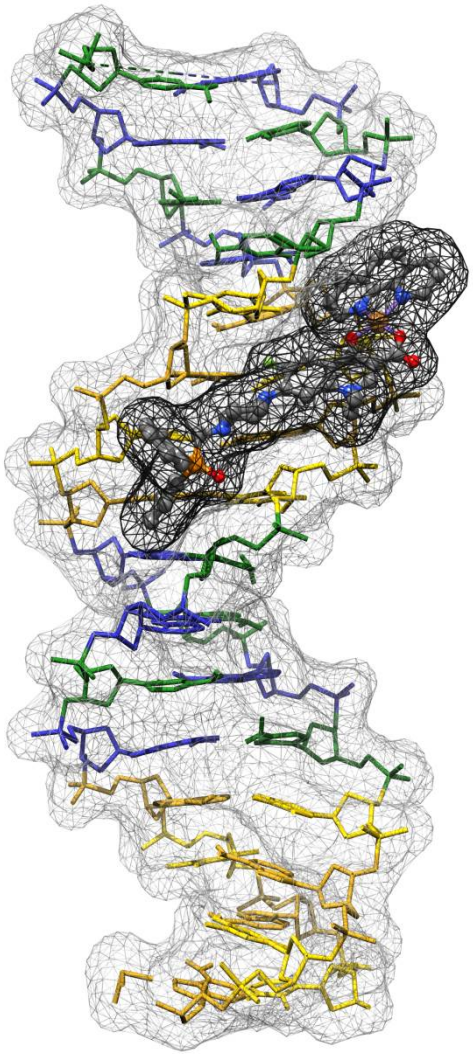
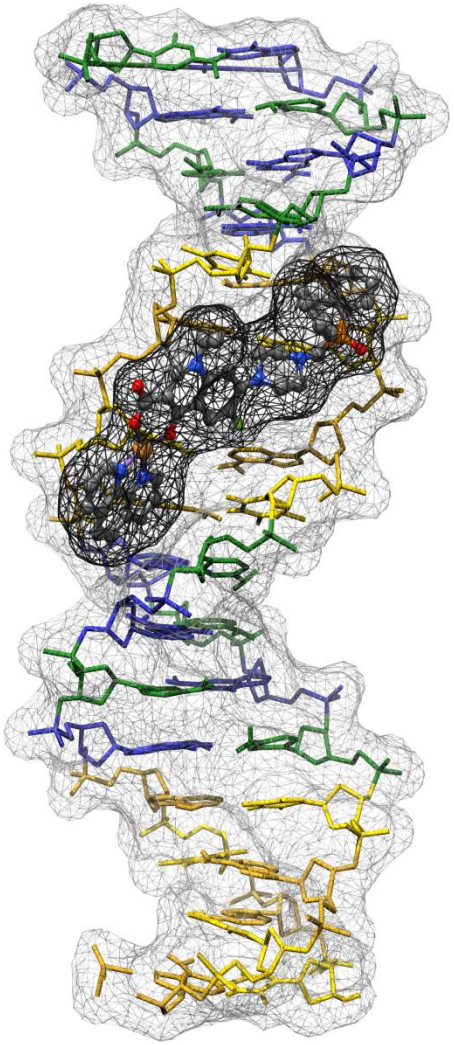


Figure S15. Molecular docking: the docking of **[OPNr-Cu^{II}]$^{+}$** (with the scoring function result)

B-DNA: -11.1



B-(AT...AT): -9.6



B-(GC-GC): -9.7

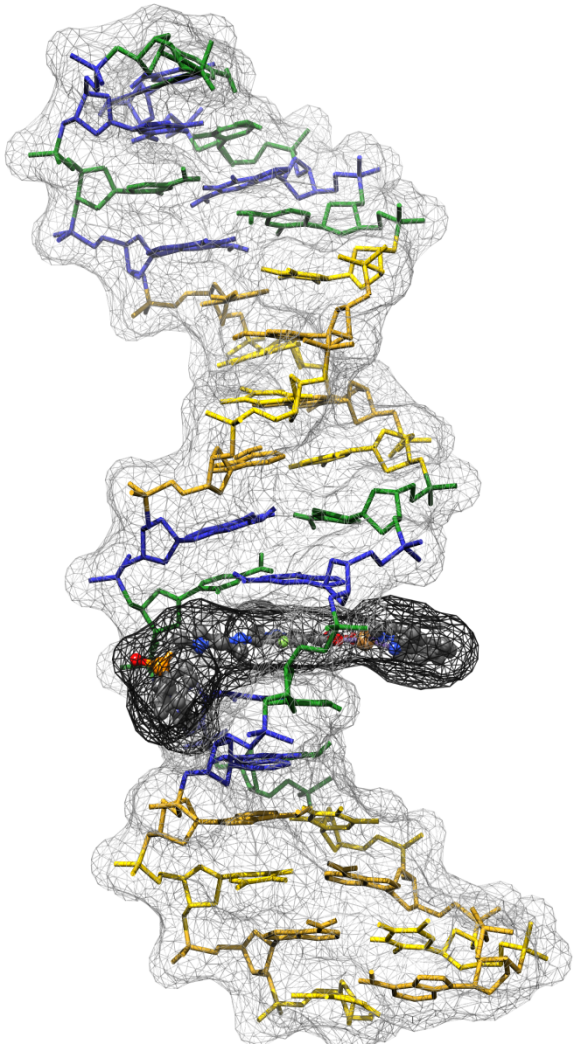
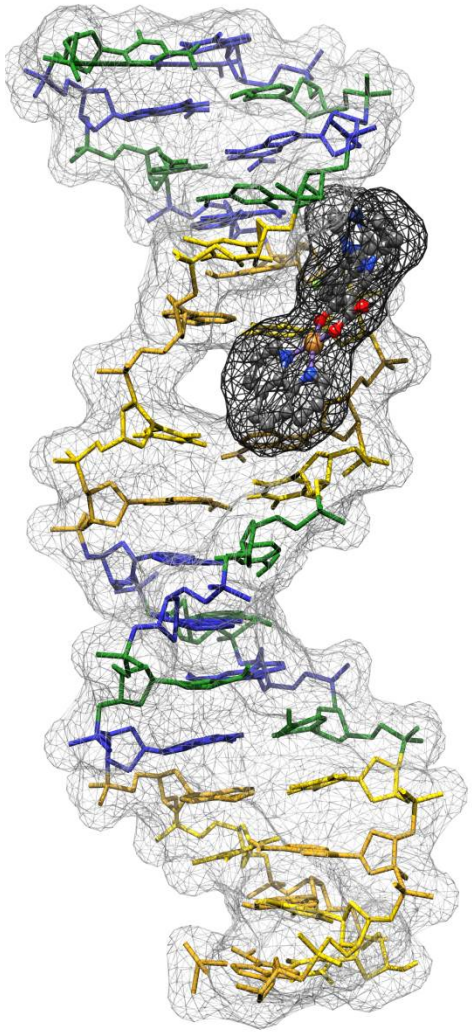
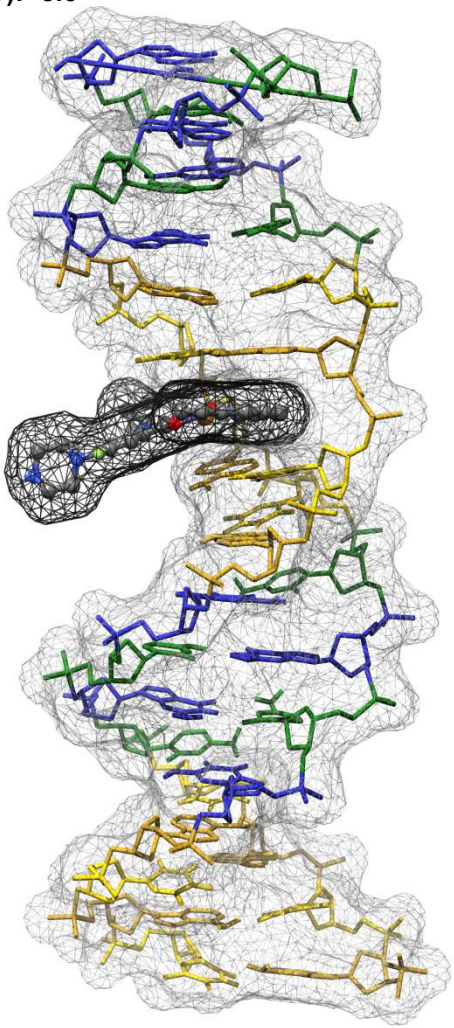


Figure S16. Molecular docking: the docking of **[HCp-Cu^{II}]$^{+}$** (with the scoring function result)

B-(AT...AT): -8.7



B-(AT...AT): -8.6



B-(GC-GC): -10.0

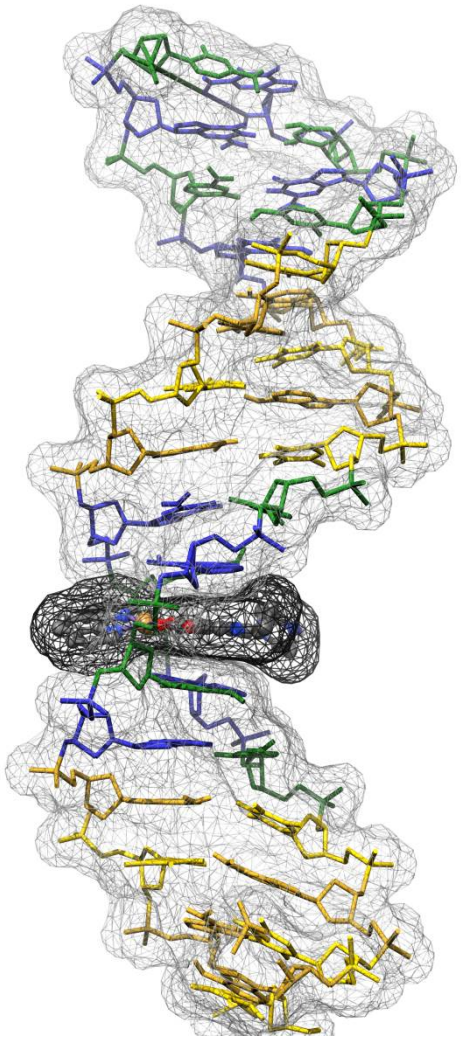
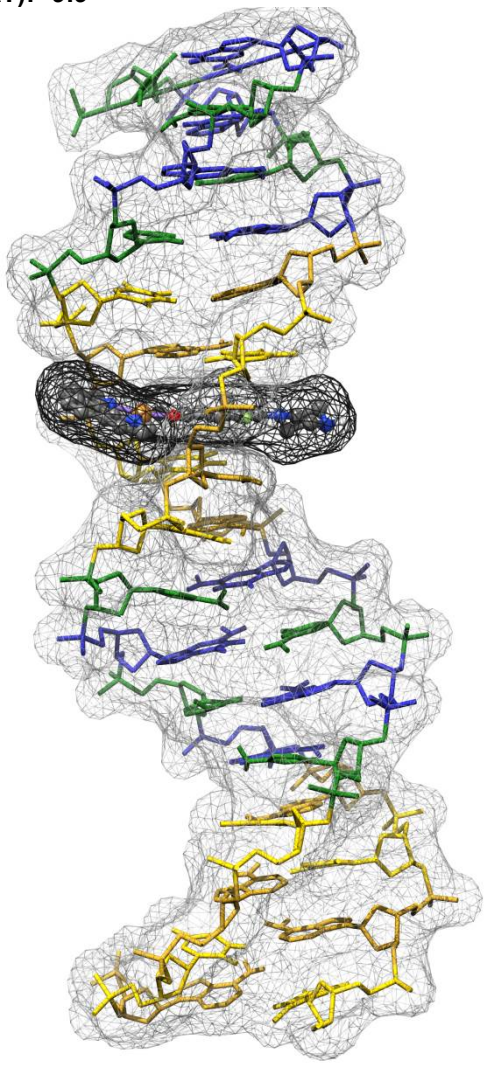


Figure S17. Molecular docking: the docking of **[HNr-Cu^{II}]$^{+}$** (with the scoring function result)

B-(AT...AT): -9.9



B-(GC-GC): -9.9

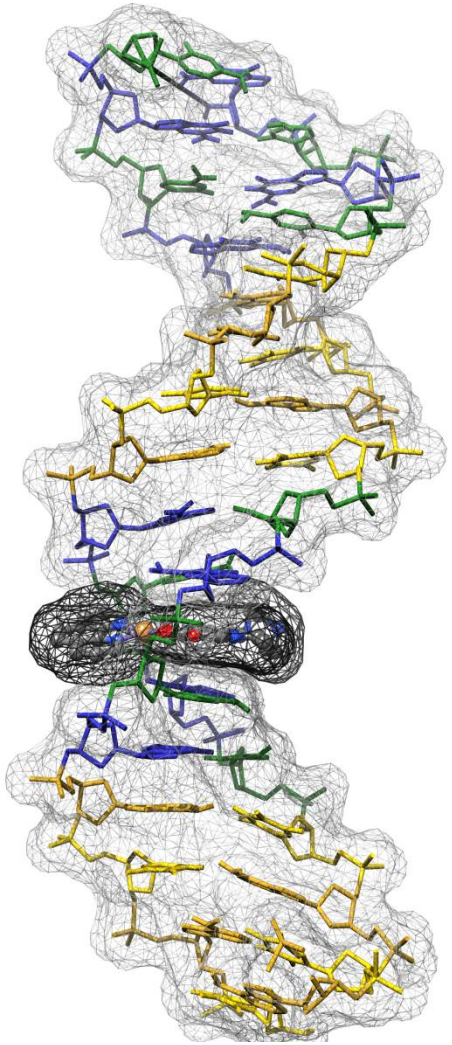


Figure S18. Molecular docking: the docking of **[Cu^{I}-POH]**$^{+}$ (with the scoring function result)

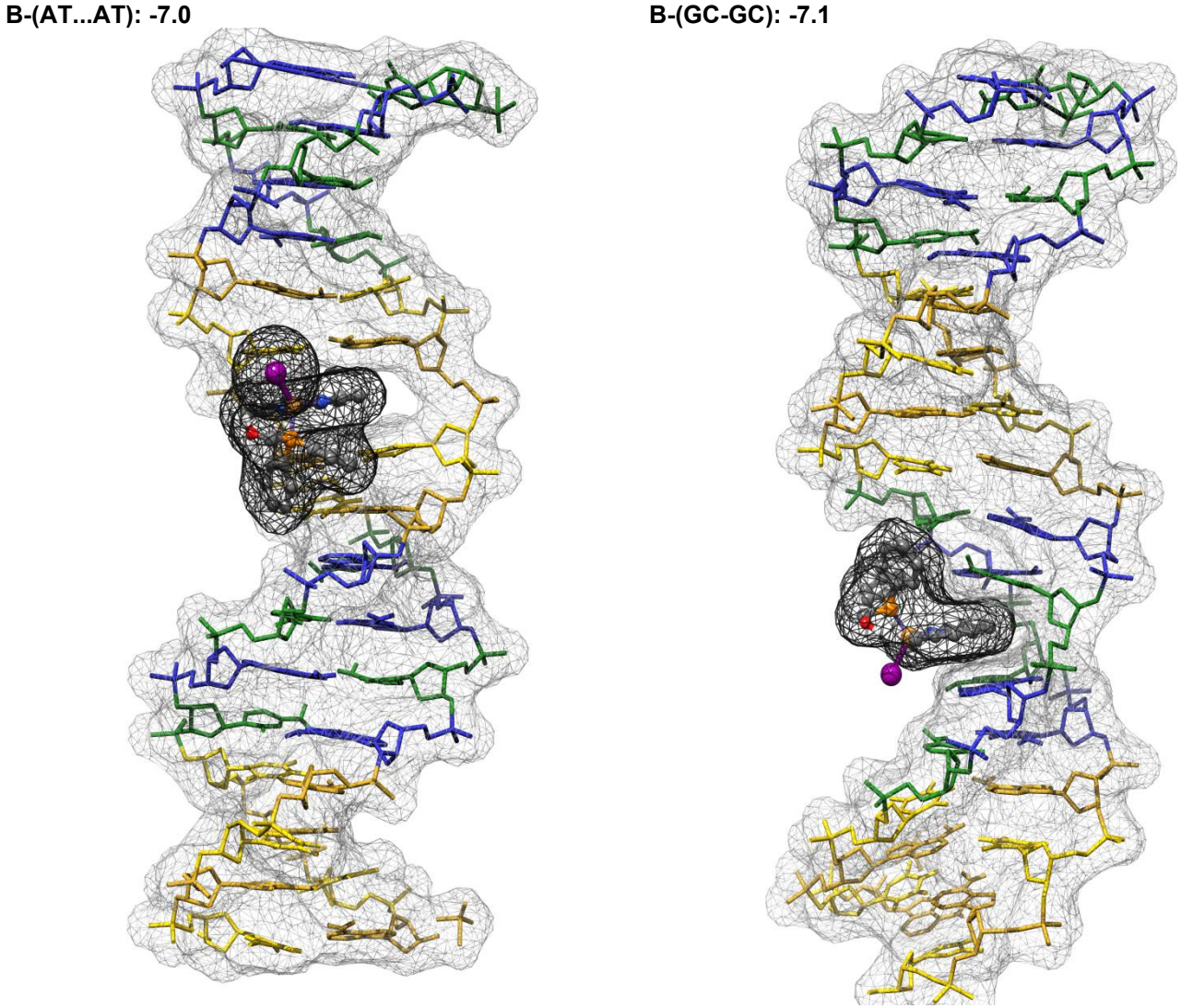
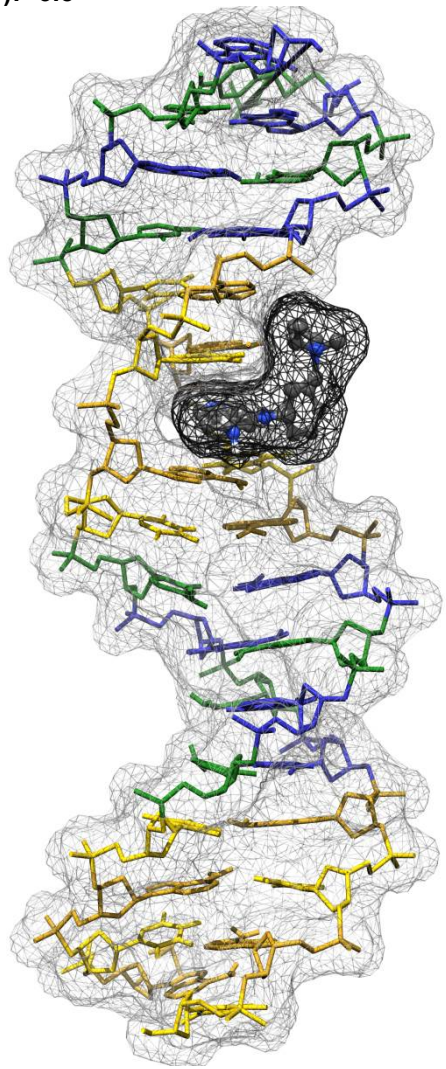


Figure S19. Molecular docking: the docking of **PI** (with the scoring function result)

B-(AT...AT): -6.5



B-(GC-GC): -6.5