Metal-DNA electronic hybridization from first principles

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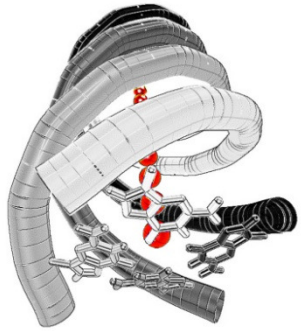
DNATEC09, May 11-15, 2009
MPIPKS Dresden, Germany

nanoStructures and bioSystems at Surfaces

DNA NANODEVICES
FP6-029192

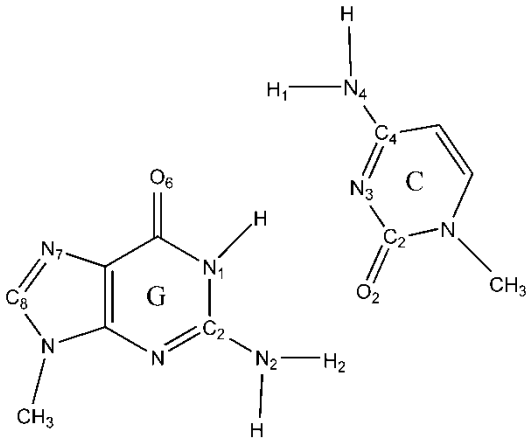


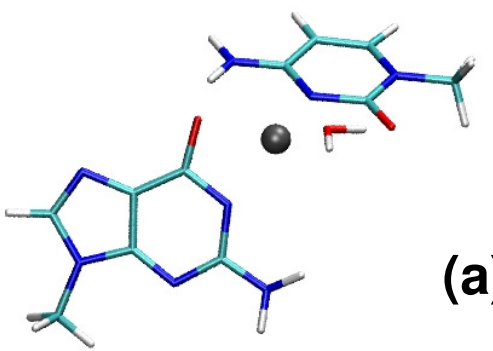
Introduction: M-DNA

♦ M-DNA is investigated for serving as novel molecular nanowires.

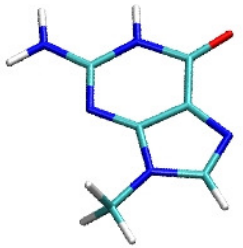
The changes induced by metal incorporation could possibly confer metal-based functionalities to DNA resulting e.g. in enhanced conductivity

♦ M-DNA is obtained from the complexation of one metal ion per base pair





(a)



(b)

Model structures proposed by

Lee (a): *Phys. Rev. Lett.,* ***2001***, 86, 3670

Fuentes-Cabrera (b): *J. Phys. Chem. B,* ***2007****, 111, 870*

Questions:

Which metal elements are most suitable to perturb the electronic structure of DNA in a profitable way for nanotechnology applications?

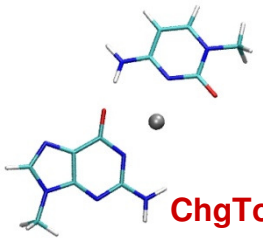
Which kind of perturbations do the metals induce? What is the effect on energy gaps?

Zn(II), Ag(I), Cu(I) and Cu(II)

investigated cations

Brancolini, G.; Di Felice, R. *J. Phys. Chem. B* **2008**, *112* (45), 14281

M-GC bp Optimized Structures

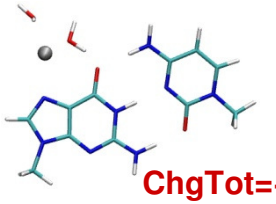


ChgTot=0

Ag(I)-imino

ChgTot=+1

Ag(I)-N7



ChgTot=+1

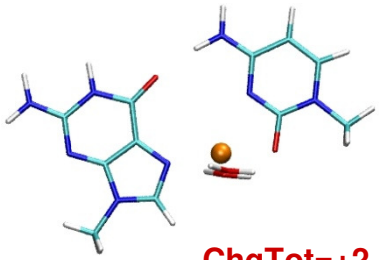
Ag(I)-N7-$2H_2O$

ChgTot=+1

Cu(II)-imino

ChgTot=+2

Cu(II)-N7

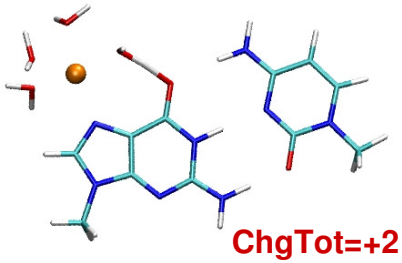


ChgTot=+2

Cu(II)-lipsyn-$2H_2O$

ChgTot=+1

Cu(II)-imino-$2H_2O$

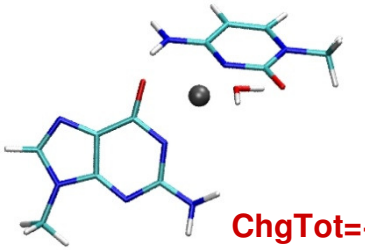


ChgTot=+2

Cu(II)-N7-$4H_2O$

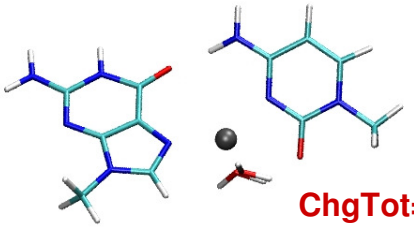
ChgTot=+1

Cu(I)-N7



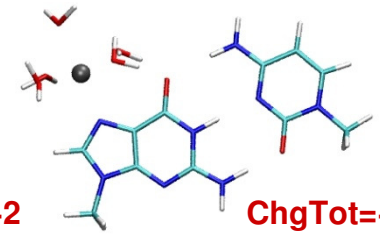
ChgTot=+1

Zn(II)-imino-H_2O



ChgTot=+2

Zn(II)-lipsyn-$2H_2O$



ChgTot=+2

Zn(II)-N7-$5H_2O$

Fully optimized structures by DFT/B3LYP

Planarity is a criterion for choice

Methods

♦**Ground-state** properties: Density Functional Theory **(DFT) codes** with localized basis sets. **Gaussian03, NWCHEM**

Tests on different xc functionals and basis sets for M-DNA

xc= B3LYP, PBE0, BHH
Std basis 6-311++G**: **Cu(II)-bp**
Std basis 6-31G**: **Zn(II)-, Cu(I)-bp**
Std basis 3-21G** 5d: **Ag(I)-bp**

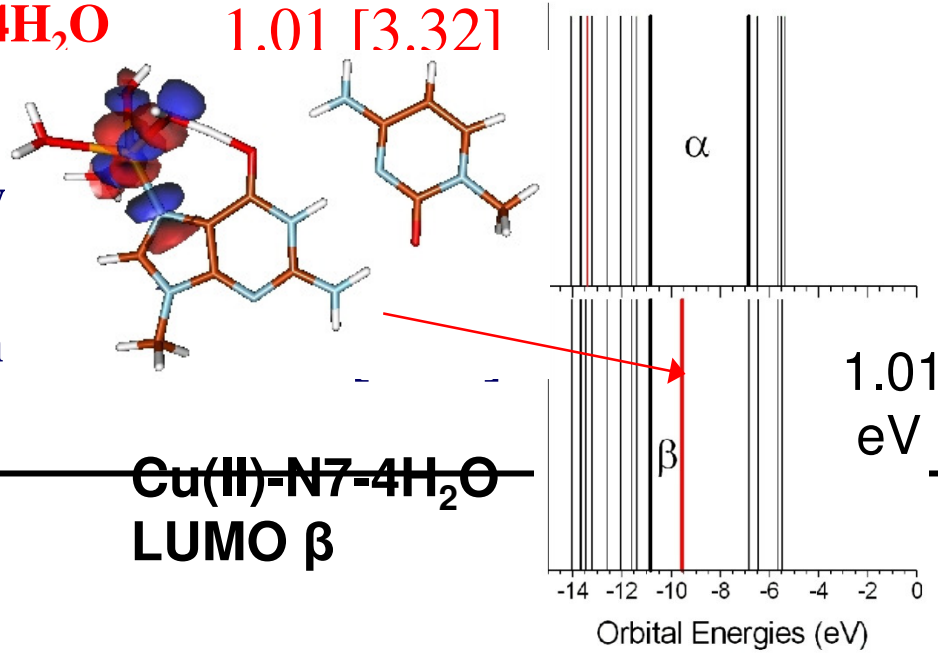
♦ **Bulk solvent** effects included through the **PCM** model in Gaussian03

Brancolini, G.; Di Felice, R. *J. Phys. Chem. B* **2008**, *112* (45), 14281

Shrinking of the excitation gap for all **Cu(II)-bps**

Largest decreases found for **Cu(II)-N7 bp**

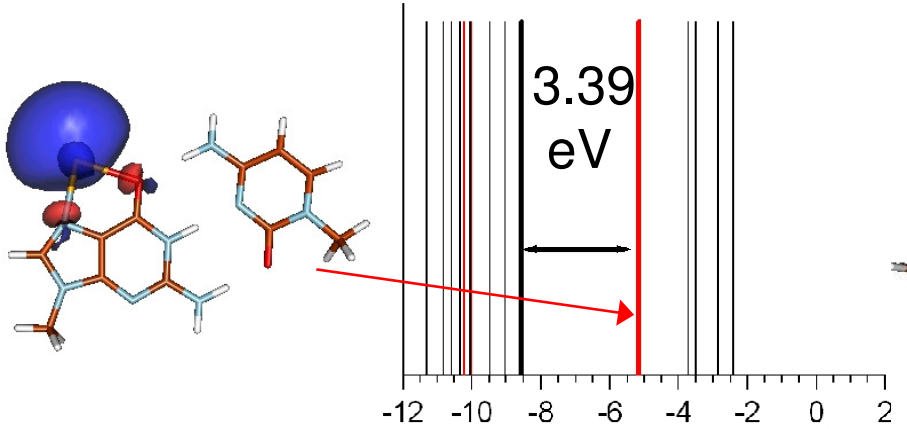
Structures M-DNA	HOMO – LUMO GAS B3LYP[eV]	[SOMO – LUMO] gaps GAS PBE0	SOL B3LYP
H-GC	3.75 **B3**	4.19	4.47
Cu(II)-N7	0.65	0.83	1.37
Cu(II)-N7-4H,O	1.01 [3.32]		2.12
Cu(II)-lipsy			
Cu(II)-imin			1.99



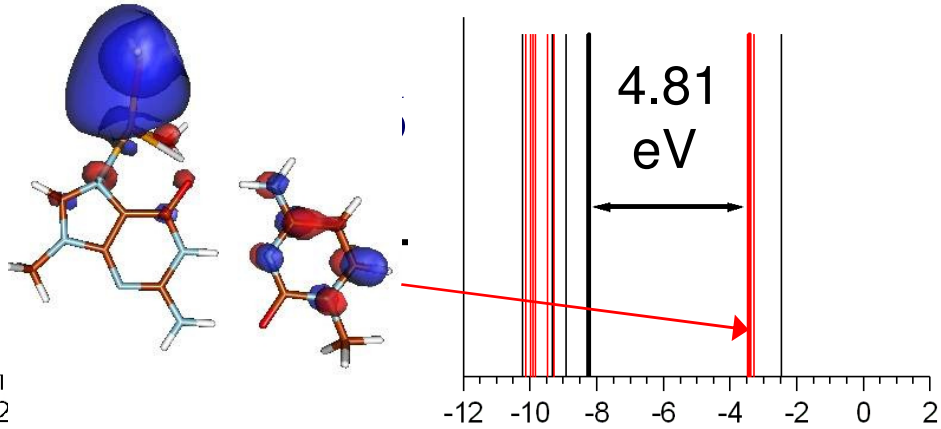
~~Cu(II)-N7-4H$_2$O~~
LUMO β

Structures	HOMO – LUMO GAS B3LYP[eV]	GAS PBE0	SOL B3LYP
H-GC	3.78	4.19	4.47
Ag(I)-N7	3.39	4.05	4.39
Ag(I)-N7-2H_2O	4.81	5.20	4.93

Excitation gap lowers in most cases



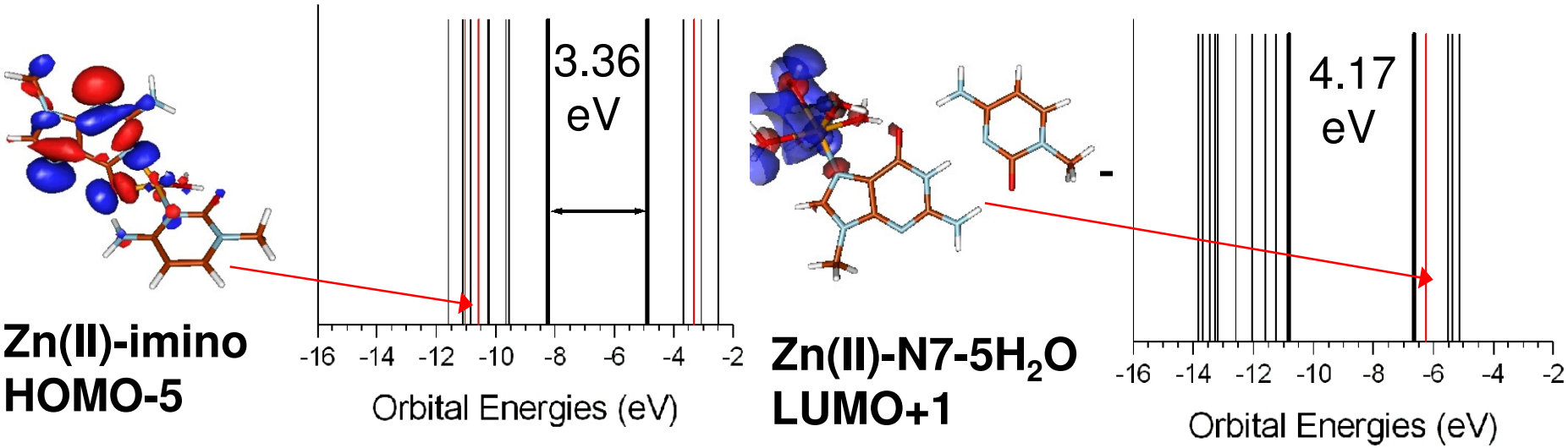
Ag(I)-N7 LUMO



Ag(I)-N7-2H_2O LUMO

Widening of excitation gap in most cases, shrinking only in **Zn-imino** case

Structures M-DNA	HOMO – LUMO GAS B3LYP[eV]	GAS PBE0
H-GC	3.79 [B2]	4.19
Zn(II)-imino-H_2O	3.36	3.75
Zn(II)-N7-5H_2O	4.17	4.59

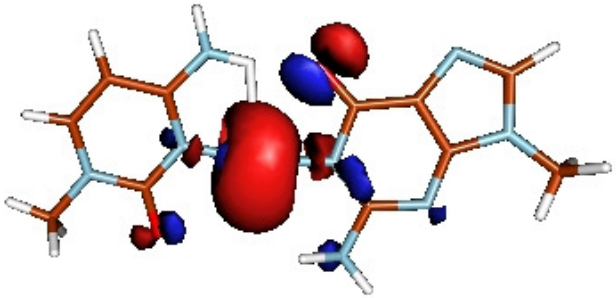


Zn(II)-imino HOMO-5

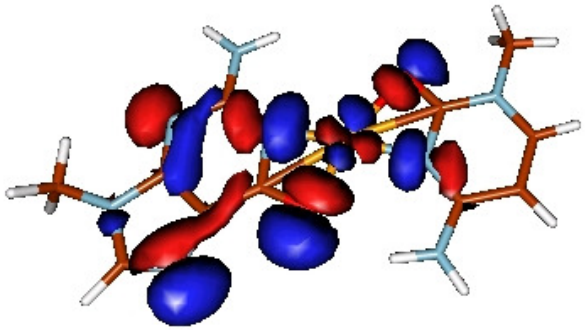
Zn(II)-N7-5H_2O LUMO+1

Electronic Structures: Cu(I,II) cations mostly contributes to the hybridization of the frontier orbitals

Closed-shell Cu(I): HOMO-1	Open-shell Cu(II) cations systems: SOMOs



Cu(I)-imino



Cu(II)-imino

Cu(II)-lipsyn-2H_2O

- The Singly Occupied Molecular Orbital (SOMO) has the same character as the β-LUMO and hosts the unpaired electron

- The SOMO is likely to be the most reactive orbital of those systems

Conclusions on M-DNA bps

Structure and electronic properties of metal modified GC bp have been investigated by *ab initio* DFT method

Doping with Cu(II) is both structurally/energetically feasible (persistent planarity & strong hybridization of frontier orbitals)

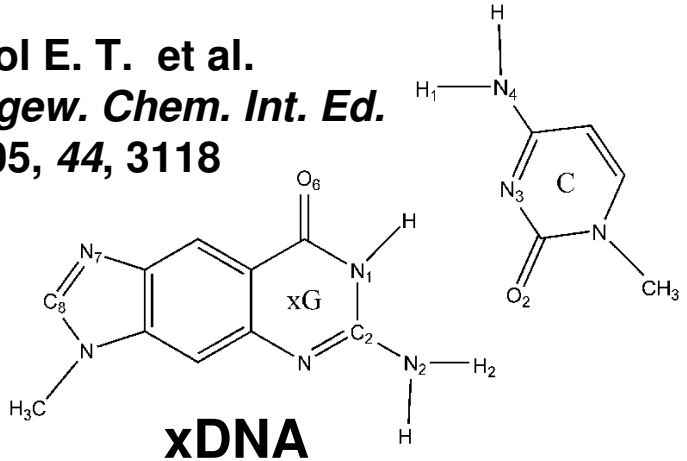
Cu-modified GC complexes might be the best candidates for nanowires with good conduction properties and on-purpose modifications of DNA to detect local electrical signals along the helix

In particular, due to the smallest HOMO-LUMO gap, Cu(II)-N7 conformation may have enormous impact in practical applications

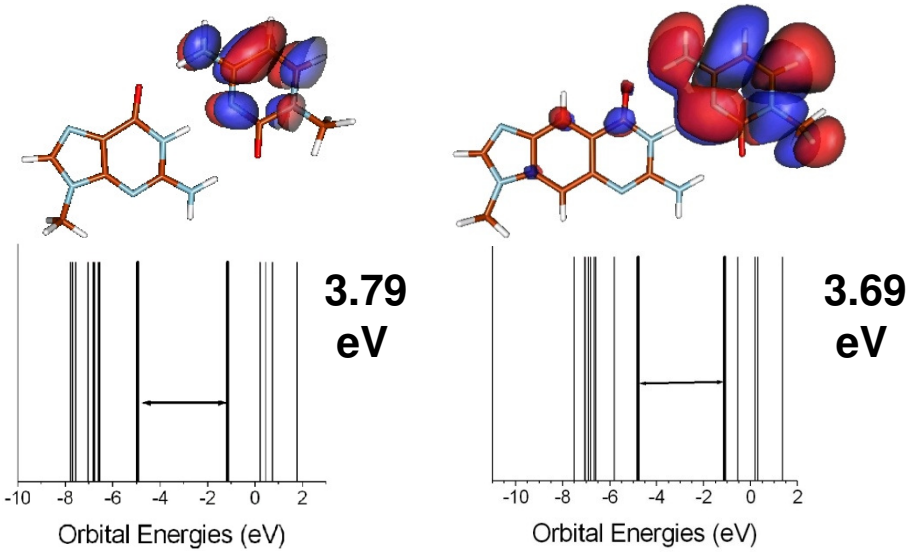
xDNA

- x-DNA: design and syntesis of more conductive structures by chemical modifications of nucleobases as an alternative way to go beyond the limits of native-DNA
- x-DNA is obtained by the expansion of each natural base with a benzene ring that is covalently bonded to the base and co-planar with it

Kool E. T. et al.
Angew. Chem. Int. Ed.
2005, *44*, 3118



xDNA



3.79 eV

3.69 eV

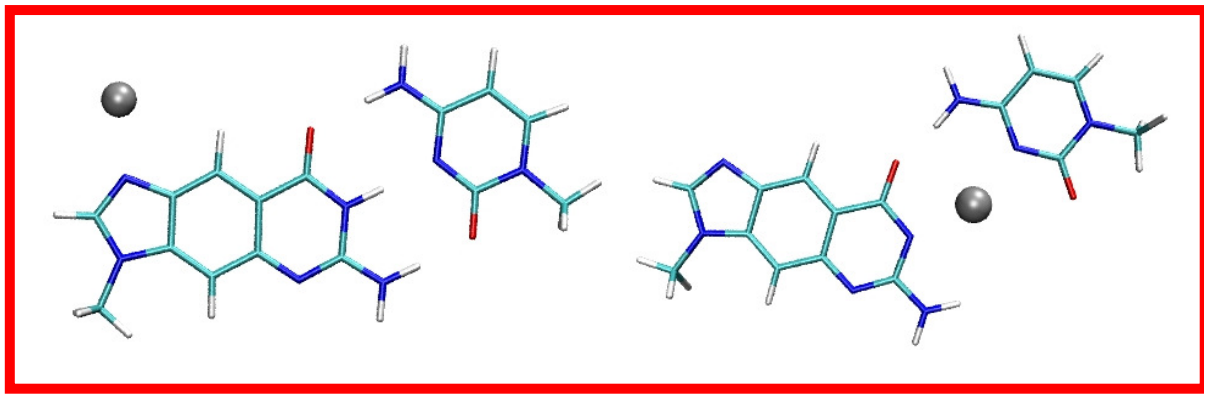
How is the aromatic enhancement reflected on the electronic/optical properties ?

Varsano, D.; Garbesi, A.; Di Felice, R. *J. Phys. Chem. B* **2007**, 111, 14012

Introduction: M-xDNA

The **combination of metal-doping and aromatic insertion** may produce a strong gap modulation?

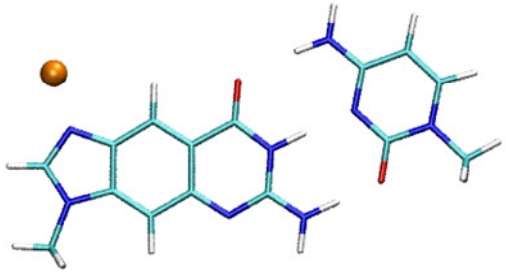
N7 and Imino:
selected structures



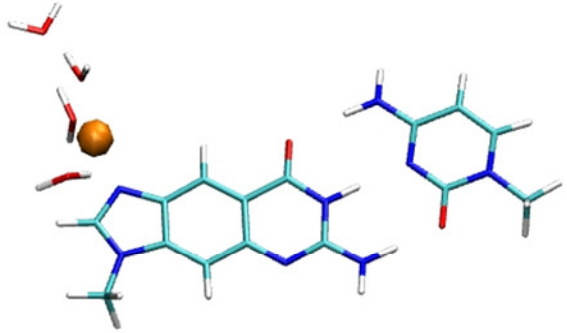
Ag(I)

Cu(II)
investigated cations

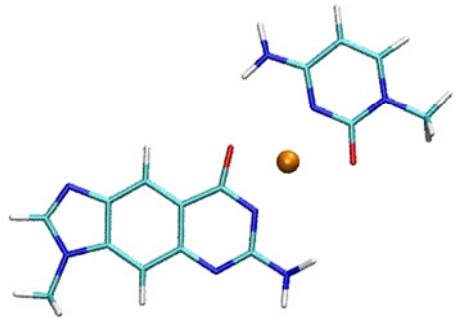
M-xGC bp Optimized Structures



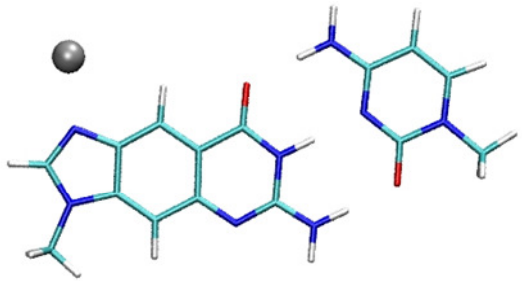
Cu(II)-CxG-N7



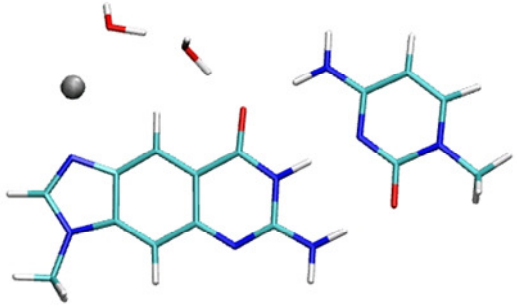
Cu(II)-CxG-N7 $4H_2O$



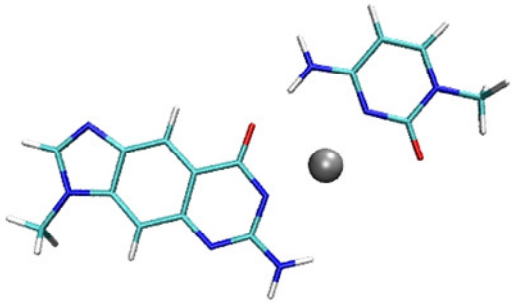
Cu(II)-CxG-imino



Ag(I)-CxG-N7



Ag(I)-CxG-N7 $2H_2O$



Ag(I)-CxG-imino

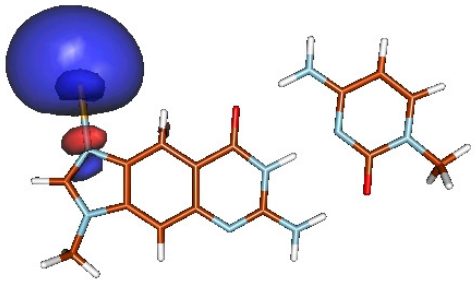
In both natural and size-expanded **bp** pairs, **Cu(II)** is the cation that mostly reduces the **HOMO-LUMO gap**, and the effect of the solvent is small.

The effect of guanine expansion is larger in Ag(I)-xGC than in Cu(II)-xGC

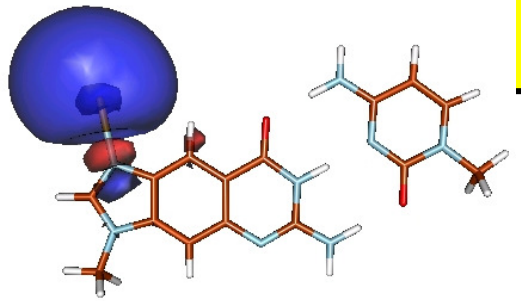
Solvent effect is to generally **open** the band gap

HOMO and **LUMO** of **Ag(I)-N7** are not alterec by the presence of the solvent, the **electron energy level shift** is associated to purely **electrostatic effects**

Structures	GAS B3LYP	GAS PBE0	SOLVENT B3LYP
H-xGC	3.65	4.00	4.24
Cu(II)-N7	0.85 [1.90]	1.20	1.11
	1.46	2.15	3.68

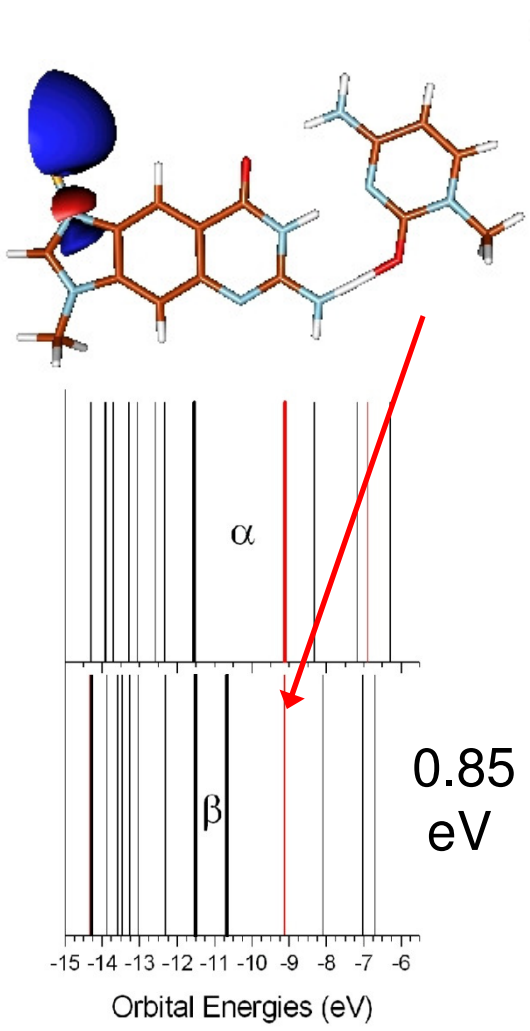


Ag(I)-N7 LUMO (GAS)

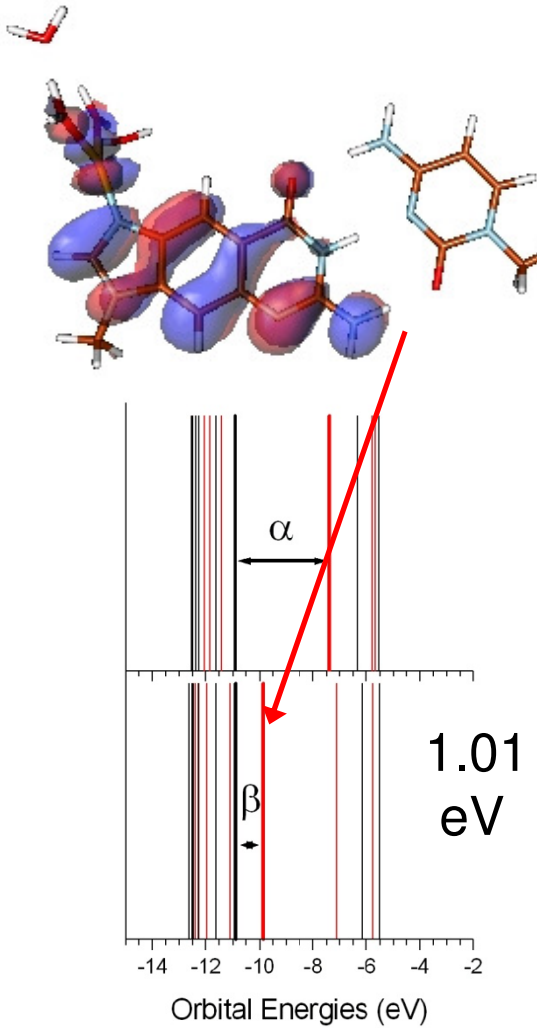


Ag(I)-N7 LUMO (SOL)

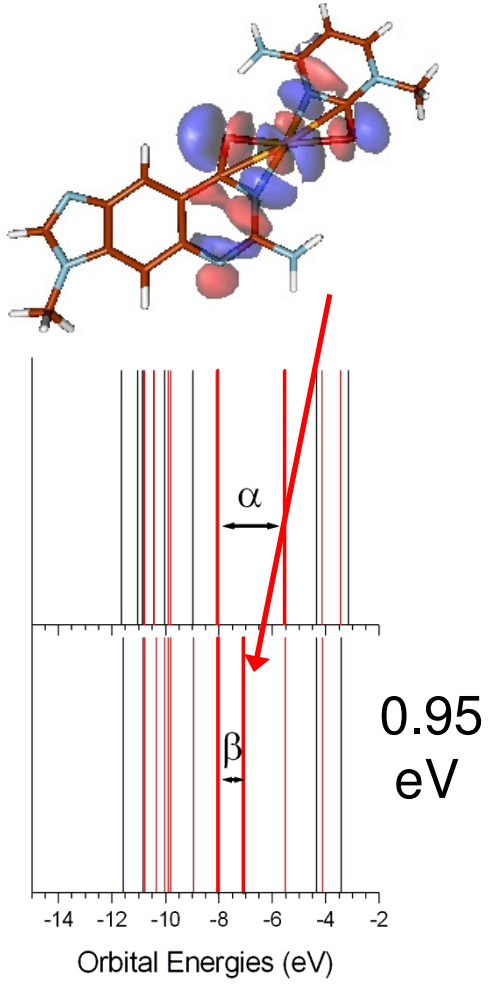
Electronic Structure of Cu-complexes



Cu(II)-xGC-N7



Cu(II)-xGC-N7-4H_2O



Cu(II)-xGC-Imino

Results on M-xDNA

Aromatic base expansion favour Planarity:
planar models are more suitable for building antiparallel duplexes

- **The effect of guanine expansion is larger in Ag(I)-xGC complexes for what concern electronic levels shifts**
- **Cu-modified xGC complexes are the most promising candidates for nanotecnology applications**

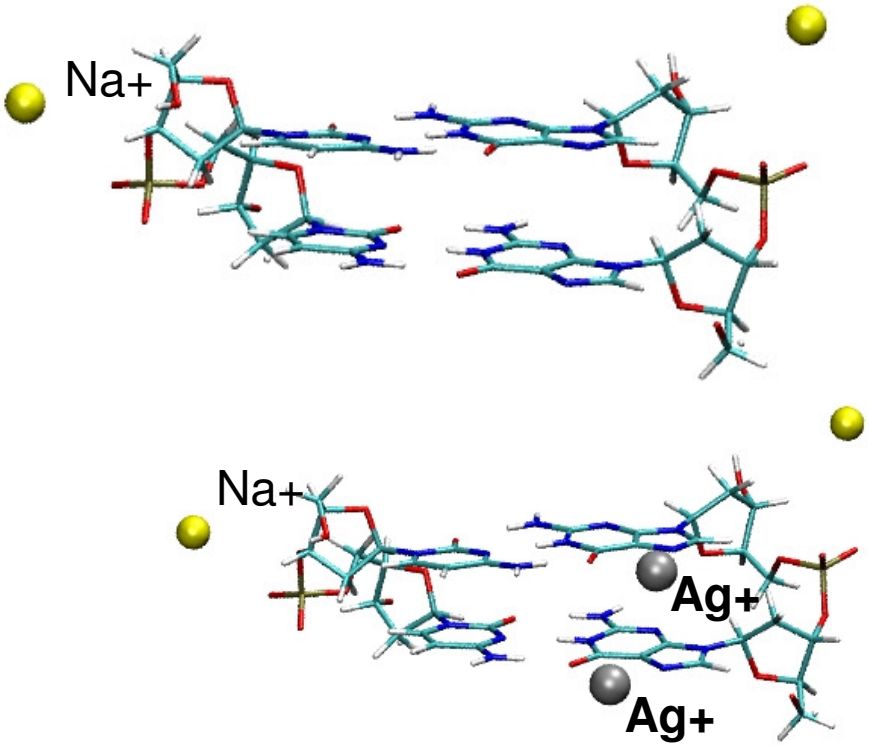
Conclusions and Perspectives

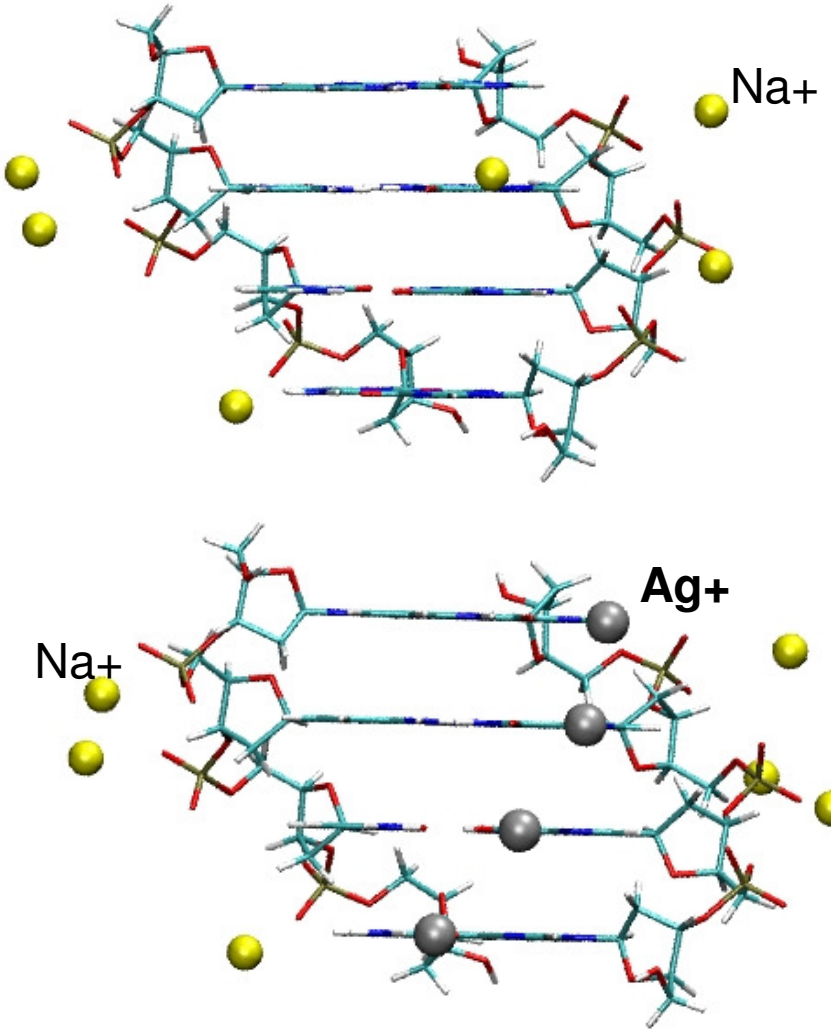
- **Cu(II) mostly contributes to the hybridazation of the frontier orbitals in both natural and size-expanded DNA base pairs.**
- **Hybridization along with persistent planarity of Cu(II)-complexes: powerful tool to design modifications exploitable in applications**
- **General shrinking of the HOMO-LUMO gap also with Cu(I), Ag(I)**

Next…

1. **Effects of stacking interactions**
2. Modifications induced by the water solvent
3. Evaluation of transfer integrals
4. Effects of structural fluctuations

On-going work on M-DNA stacks





- **Electronic structures**, HOMO-LUMO gaps
- Comparisons between different **exchange-correlation** functionals (B3LYP, PBE0, BHH) and basis sets crucial for base-pairs including transition metals
- Effects of **stacking** interactions

Stability: Binding Energies (storage)

M-DNA

Dimer models	E^{dimer}	E^{BSSE}	ΔE^{Def}	$\Delta E^{binding}$
Cu(I)-imino	-2655.9024653	-2655.81071	-0.0195	-45.26
Cu(II)-imino	-2655.7040626	-2655.56258	-0.0163	-78.47
Cu(II)-imino-$2H_2O$	-2808.6024233	-2808.49226	-0.0567	-33.52
Ag(I)-imino	-6186.0390459	-6185.97552	-0.0097	-33.77
Zn(II)-imino-H_2O	-2871.0263726	-2870.89559	-0.0256	-65.96
Trimer models	E^{trimer}	E^{BSSE}	ΔE^{Def}	$\Delta E^{binding}$
Cu(II)-N7	-2655.9096433	-2655.35142	-0.0301	-331.20
Cu(II)-N7-4aH_2O	-2961.8126735	-2961.49253	-0.0988	-138.81
Cu(II)-N7-4bH_2O	-2961.8062325	-2961.54184	-0.0664	-124.18
Cu(II)-lipsyn-$2H_2O$	-2808.9229342	-2808.54107	-0.0364	-216.64
Ag(I)-N7	-6186.4821938	-6186.29401	-0.0195	-105.76
Ag(I)-N7-H_2O	-6262.5396345	-6262.37255	-0.0181	-93.43
Ag(I)-N7-$2H_2O$	-6338.5870565	-6338.43217	-0.0434	-69.91
Zn(II)-N7-$5H_2O$	-3177.1284545	-3176.89228	-0.0656	-106.97
Zn(II)-lipsyn-$2H_2O$	-2947.7932534	-2947.41262	-0.0523	-205.88

M-xDNA

Model M-xGC	E^{dimer}	E^{BSSE}	ΔE^{Def}	$\Delta E^{binding}$
Cu(II)-imino	-2809.82605425	-2809.67167575	-0.035811641	-74.35
Ag(I)-imino	-6338.77299730	-6338.70755831	-0.011356642	-33.91
Model M-xGC	E^{trimer}	E^{BSSE}	ΔE^{Def}	$\Delta E^{binding}$
Cu(II)-N7	-2810.08610154	-2809.47533717	-0.027127084	-366.00
Ag(I)-N7	-6339.17323369	-6339.01828347	-0.093688609	-38.41
Ag(I)-N7-$2H_2O$	-6491.37184000	-6491.11138053	-0.147396209	-8.19

Formation energies with respect to the constituens isolated parts

Among imino: Cu(II)-imino has the highest energy gain

Among N7: Cu(II)-N7 has the markedly highest energy gain