C.N.R. – INFM
Istituto Nazionale per la Fisica della Materia
nanoStructures and bioSystems at Surfaces

Al Consiglio Nazionale delle Ricerche
Direzione Generale, Ufficio Paesi Industrializzati e Organismi Internazionali
Programma Short-Term Mobility
Piazzale LAdo Moro 7, 00185 Roma

Oggetto: relazione scientifica finale per la liquidazione di missione short-term mobility, missione CNR-INFM MO156/08

Proposed activities.

(1) Density-Functional Theory electronic structure calculations of chemical modifications (H replacement with CH3 or halides, coupling with transition metal ions) of synthetic nucleotides and nucleotide-pairs of the xDNA kind, which include an aromatic ring co-planar with the natural base. It was observed that xDNA has enhanced stacking behavior with respect to natural DNA (higher π-π superposition due to the presence of the benzene rings). This feature may be exploited for developing DNA-based self-assembling nano-devices and nano-circuits. The expansion of the genetic alphabet is a further fascinating application.
(2) Analysis of results: which alterations are most promising for modulating the HOMO-LUMO gap? Which technical details ensure a reliable accuracy of the results (xc functional, basis set)?
(3) Preparation of a draft joint manuscript. Discussions of future joint projects.

Work performed.

The work was very successful and went even farther the intended plan, especially for the established prospect towards future projects. I list below the achievements within each of the 3 tasks above.

I worked daily with my host Miguel Fuentes-Cabrera. The work consisted of: discussions, carrying out calculations, analyzing the results. The trip was planned to complement the remote communications in the framework of an active joint computational project between myself and my host, running since March 2008 and funded by the Center for Nanoscale Materials Science CNMS) at Oak Ridge National Laboratory (ORNL).

At the beginning of my stay, I got acquainted with the NERSC (Berkeley) and ORNL (Oak Ridge) supercomputers to which the joint computational project gave me access and computational time, with the software installed on these computers, and with the submission/running procedures. The computers that I used for this project were bassi.nersc.gov (IBM SP5) and cnms.oic.ornl.gov (PC cluster).

I already had an account on bassi.nersc.gov before the trip but never used it, whereas my collaborator Giorgia Brancolini performed calculations there and on other NERSC parallel computers.

Access to cnms.oic.ornl.gov is severely restricted by US Government (Department of Energy, DoE) security rules and was hindered before the trip by unclear explanations of the request procedure, in particular about the distribution of a “token” for random passwords for remote access and about the password setting rules. The on-site stay allowed me to quickly solve all these problems, with the constant help of my host and other ORNL personnel: I had the username and password and token for myself, and the token for my collaborator Giorgia Brancolini, who has now also been able to establish a connection to this computer after my return and explanations of the various needed steps. Hence, one notable successful result of my trip is that now my collaborators and I can use the supercomputers at CNMS, which are a precious computational resource for my research activities.

(1) Electronic structure calculations were carried out with the NWChem/Gaussian (localized basis-set functions, for isolated molecules) and PWscf (plane-wave basis set, adopted for periodic stacks) softwares. The relative performance of the two methods was tested on the isolated x-guanine (xG) base.
   a. We first decided to focus on the following chemical modifications: (i) substitution of a cyclo-H in xG with a halogen atom, we considered both F and Cl substitutions; (ii) complexation of a xG-C pair with Ag and Cu metal ions; (iii) selenated thymine (Se-T). We decided to look at DFT results not only in terms of HOMO-LUMO gap, but also in terms of band-widths and band-gaps of artificial periodic stacks with variable twist angles.
   b. I carried out NWChem calculations on isolated xG with F and Cl substitutions, on the PC cluster cnms.oic.ornl.gov.

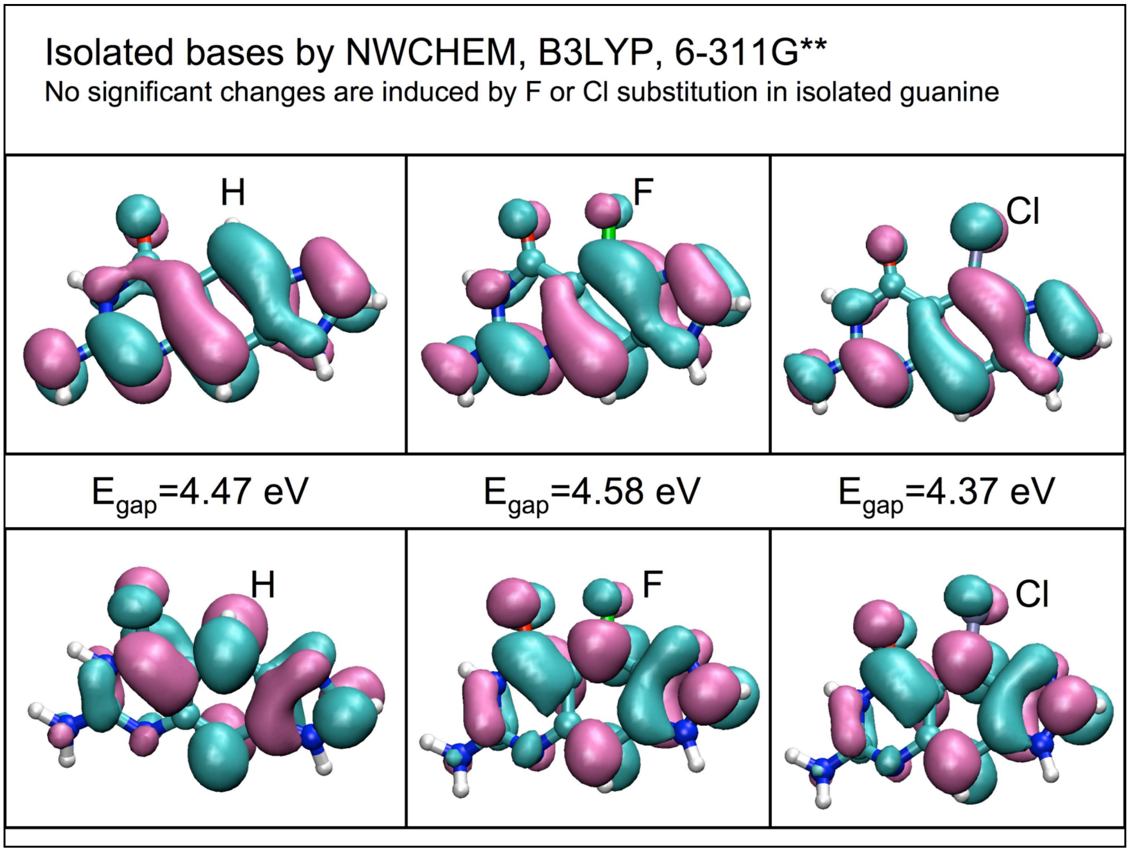


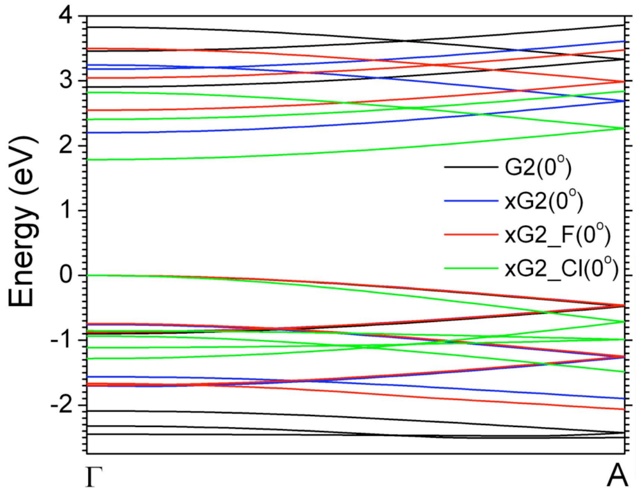
Figure 1. Highest Occupied Molecular Orbital (HOMO, top row) and Lowest Unoccupied Molecular Orbital (LUMO, bottom row) of xG (left), F-substituted xG (F-xG, middle) and Cl-substituted (Cl-xG, right). The corresponding values of the HOMO-LUMO gap are reported.

c. I carried out PWscf calculations on periodic xG stacks, with 0 and 36 degrees twist angles, with and without substitutions of H by F and Cl in the benzene ring.
d. I carried out PWscf calculations on periodic Se-T, with 0 degrees twist angle.
e. Calculations on metalated xG-C pairs were already done before the trip by my collaborator Giorgia Brancolini, and they were part of the analysis and discussion of general trends.

(2) The results are reported here according to items b-e above. They were discussed onsite with Miguel Fuentes-Cabrera and Bobby Sumpter, and furhter discussion is ongoing remotely.

b. The relaxed structures and the values of the HOMO-LUMO gapes are reported in Figure 1. xG is obtained with the insertion of a benzene ring between the pentagonal and hexagonal hetero-cycles of guanine (left panels). The chemical substitutions are obtained by replacing one H atom in the benzene ring by F or Cl, respectively middle and right panels. The HOMO-LUMO gaps of the isolated molecules indicate that the chemical substitutions do not induce a gap modulation, which could be useful for nanowire and sequencing applications.

G2 and xG2 stacks by Pwscf, twist=0°
25 Ry cutoff, ultrasoft pseudo



E_{gap} (eV)	Δ_{HOMO} (eV)	Δ_{LUMO} (eV)
2.906	0.477 (0.899) $m_h^*=2.18$	0.426 (0.920) $m_e^*=2.17$
2.201	0.461 (0.873) $m_h^*=2.20$	0.488 (1.042) $m_e^*=1.90$
2.548	0.462 (0.876) $m_h^*=2.21$	0.440 (0.950) $m_e^*=2.10$
1.786	0.715 (1.281) $m_h^*=1.58$	0.482 (1.034) $m_e^*=1.92$

- m_e^* and m_h^* are the electron and hole effective masses, in units of the electron mass
- The values in parentheses are the values relative to the “folded” bands because of the double degeneracy

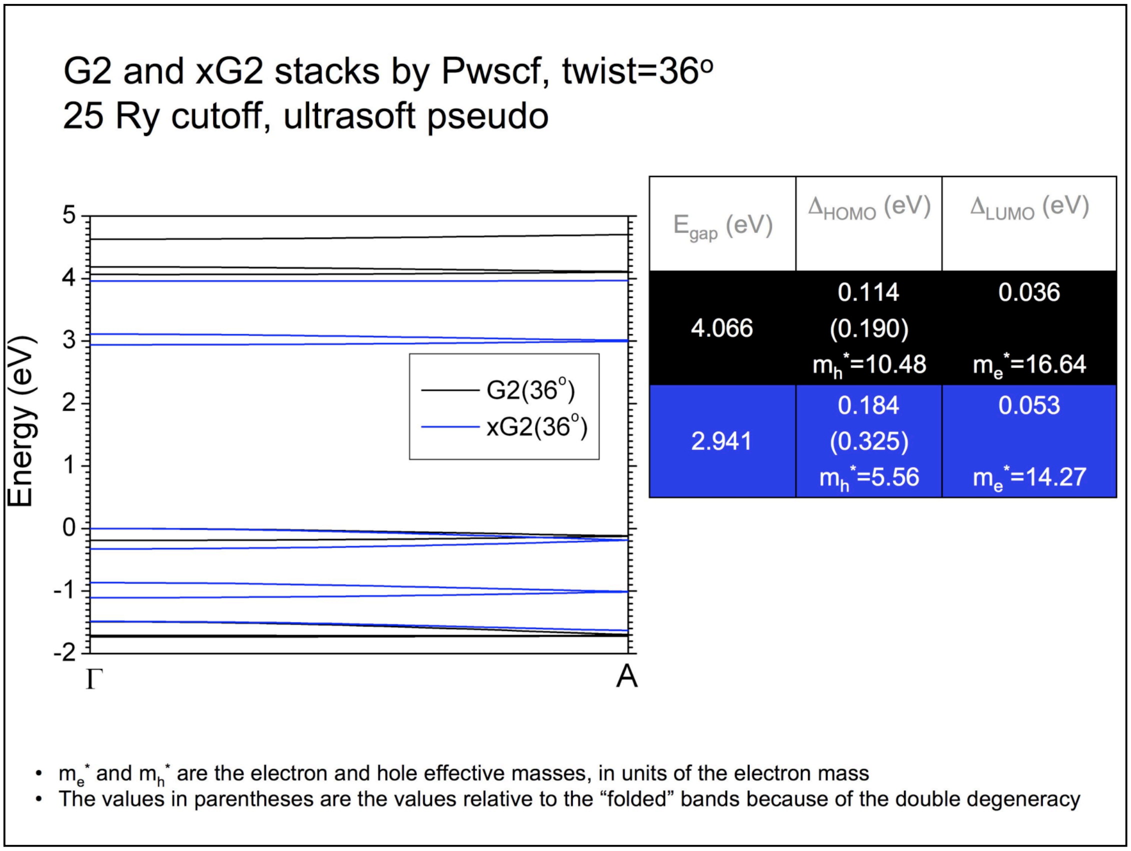
Figure 2. (Left) bandstructure plot for periodic stacks of eclipsed guanines and modified guanines. The legend in the diagram explains the different curves. (Right) The table summarizes significant bandstructure parameters: the fundamental gap that derives from the molecular HOMO-LUMO gap, the amplitude of the HOMO and LUMO bands and the effective masses for holes and electrons.

However, this may be affected by stacking and H-bonding. Stacking effects are thus checked in point b.

c. The bandstructure plot for infinite periodic wires consisting of eclipsed (0-degree twist angle) G, xG, F-xG and Cl-xG is reported in Figure 2, along with a table that summarizes significant values of the gaps and effective masses. The equivalent bandstructure plot and parameter table are reported in Figure 3 for infinite periodic wires in which adjacent bases are rotated by 36 degrees. These periodic wires do not represent the real DNA helical motif but are model system to investigate the effect of twist angle variability. The fact that the wire is periodically infinite allows us to define the associated reciprocal lattice and the concept of the *bandstructure*, as alternative to the *energy level structure* of single molecules.

The critical analysis of the data reported in Figure 2 support the following observations:

- the bandgap of all the considered benzene-expanded guanines is lower than that of natural guanine; although the absolute gap value is affected by the typical underestimation of density functional theory, the relative trends are reliable;


G2 and xG2 stacks by Pwscf, twist=36°
25 Ry cutoff, ultrasoft pseudo

E_{gap} (eV)	Δ_{HOMO} (eV)	Δ_{LUMO} (eV)
4.066	0.114 (0.190) $m_h^*=10.48$	0.036 $m_e^*=16.64$
2.941	0.184 (0.325) $m_h^*=5.56$	0.053 $m_e^*=14.27$

- m_e^* and m_h^* are the electron and hole effective masses, in units of the electron mass
- The values in parentheses are the values relative to the “folded” bands because of the double degeneracy

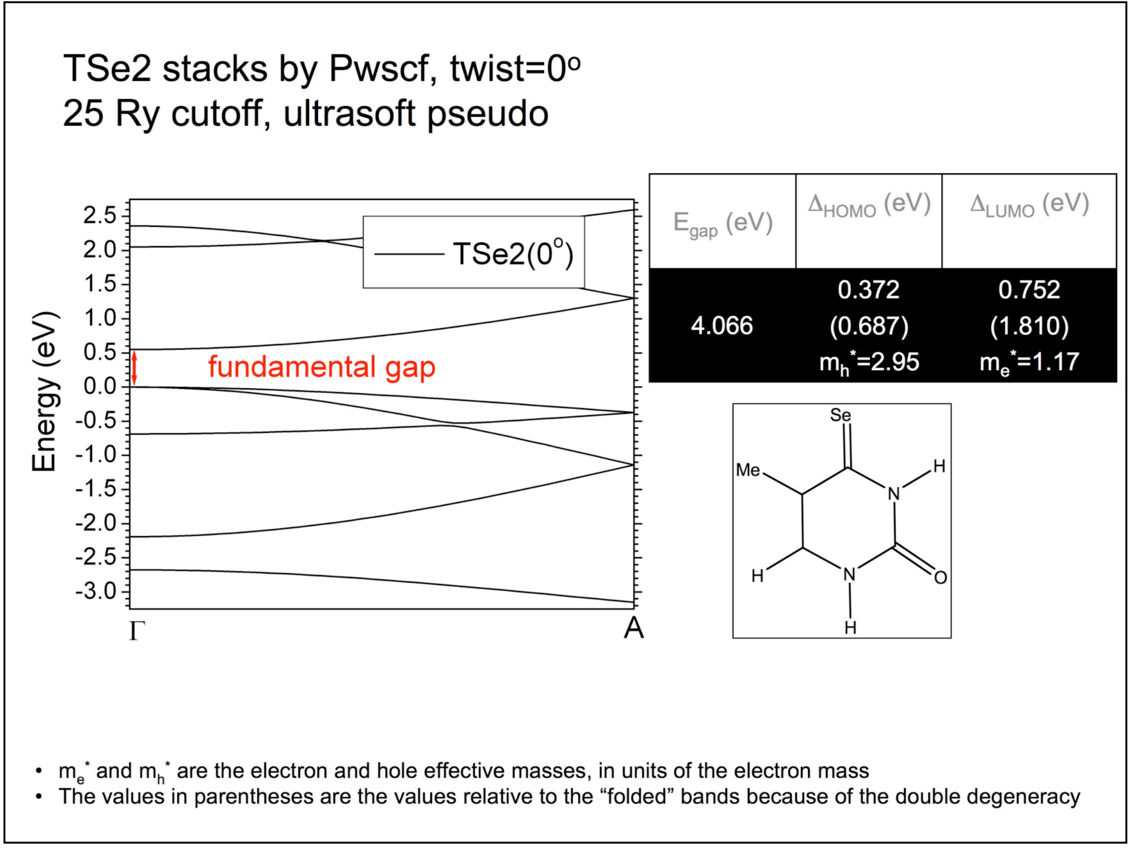
Figure 3. (Left) bandstructure plot for periodic stacks of 36-degrees-rotated guanines and x-guanines. The legend in the diagram explains the different curves. (Right) The table summarizes significant bandstructure parameters: the fundamental gap that derives from the molecular HOMO-LUMO gap, the amplitude of the HOMO and LUMO bands and the effective masses for holes and electrons.

- the bandgap shrinking is accompanied in the case of Cl-xG by an increase of the bandwidth and of the band dispersion for both the top valence and bottom conduction bands, which in turns results in smaller effective masses (namely, higher mobilities); the bandwiths and effective masses for the cases of xG and F-xG are instead very similar to those of G;

In summary, while F and Cl substitutions do not give gap modulation at the single molecule level, stacking effects induce significant variation of the bandstructure with Cl-substituted xG. Bandgap and effective-mass shrinking may be appealing for nanowire and sequencing applications.

The analysis of Figure 3 indicates that the higher twist angle (36 degrees as in real double helices) corresponds to larger bandgaps and larger effective masses, which goes in the direction opposite to that useful for transport applications. In fact, the resulting effective masses are typical of insulators. Again, as in the case of 0-degrees twist angle, the benzene expansion corresponds to a decrease of the effective masses.

As a follow up to this activity, calculations for 36-degrees-rotated F-xG and Cl-xG are ongoing now.



TSe2 stacks by Pwscf, twist=0°
25 Ry cutoff, ultrasoft pseudo

E_{gap} (eV)	Δ_{HOMO} (eV)	Δ_{LUMO} (eV)
4.066	0.372 (0.687) m_h^*=2.95	0.752 (1.810) m_e^*=1.17

- m_e^* and m_h^* are the electron and hole effective masses, in units of the electron mass
- The values in parentheses are the values relative to the “folded” bands because of the double degeneracy

Figure 4. (Left) bandstructure plot for periodic stacks of eclipsed selnated thymines. (Top right) The table summarizes significant bandstructure parameters: the fundamental gap that derives from the molecular HOMO-LUMO gap, the amplitude of the HOMO and LUMO bands and the effective masses for holes and electrons. (Bottom right) Chemical formula of selenated thymine, obtained with the replacement of the H atom attached to C6 with a Se atom.

d. The bandstructure plot for infinite periodic wires consisting of eclipsed (0-degree twist angle) T-Se is reported in Figure 4, along with a table that summarizes significant values of the gaps and effective masses and the structure of the molecule in the lower right inset.
   These results are being now compared to single-molecule calculations.
   As a follow up to this activity, calculations for 36-degrees-rotated Se-T are ongoing now.
e. Metallization of GC pairs results in gap modulation and efficient metal-base hybridization of the frontier orbitals for Cu and Ag, negligible significant effects for Zn. Metallization of xGC with Ag ions is more effective than in GC for what concerns gap reduction. Further development of this work may include the treatment of metallization of xAT pairs.

(3) General discussions.

a. Plan for two joint publications: one on selenated xT, one on chemical modifications of xG and xG-C pairs, including isolated bases, base pairs and stacks, ground-state DFT calculations, transfer integrals and bandstructure of periodic systems. We started a draft for the former manuscript. These discussions involved also Bobby Sumpter, a close collaborator of Miguel Fuentes-Cabrera at Oak Ridge, who is expert in quantum chemistry calculations and able to compute transfer integrals, with a methodology different from the one developed by my group in Modena and that can be compared.
b. Discussion of topics that may be the object of future research projects depending on the availability of suitable funding: (i) whether it is possible, and how, to reveal mismatches by electrical signals (possible relevance in detection of genetic diseases and gene therapy); (ii) correlations of local fluctuations along a double helix attached to two carbon nanotubes; (iii) x-bases and x-base stacks and derivatives.
c. Discussion of a workshop on the generation of force-fields for DNA-surface interaction. Miguel is planning to organize it at Oak Ridge and we discussed possible invited speakers and outline.
d. Discussion with scientific leaders at Oak Ridge National Laboratory: (i) Peter Cummings, CNMS principal scientist (force-field generation); (ii) Jack Wells, NTI future director (replacing Thomas Schultess), explained to me the strategy of the laboratory as a user facility, the nod structure, the inspiration to CECAM organization, and we discussed various possible mutual interest and the possibility of a joint institutional agreement for training and exchange of personnel.

Fruitrice: Rosa Di Felice Rosa Di Felice
Ricercatrice TI III livello, National Center on nanoStructures and bioSystems at Surfaces (S3) of INFM-CNR

Proponente: Elisa Molinari EMolinari
Direttrice, National Center on nanoStructures and bioSystems at Surfaces (S3) of INFM-CNR

Modena, 15 Ottobre, 2008