Al Consiglio Nazionale delle Ricerche
Direzione Generale, Ufficio Paesi Industrializzati e Organismi Internazionali
Piazzale Aldo Moro 7, 00185 Roma

CNR SHORT-TERM MOBILITY 2009

Application Period: 07/09/2009 – 29/09/2009
Applicant: Dr. Giorgia Brancolini

Purpose of the visit

The Center for Nanophase Material Sciences (CNMS) at Oak Ridge National Laboratory (ORNL) and the CNR-INFM National Research Center S3 in Modena combine a long-term expertise in using different DFT codes with plane-waves (PWSCF) and localized (NWCHEM, G03, SIESTA) basis sets, as well as molecular dynamics tools (AMBER, NAMD), for the simulation of biological systems in complex environments.
The primary purpose of the visit was to address the electronic structure of DNA-derivatives, obtained with the replacement of the H-termination of size-expanded nucleobases with chemical groups such as CN, F, CH3 or OH, potentially exploitable for nano-technological applications.
The collaboration between the applicant Giorgia Brancolini and Rosa Di Felice at S3 and Miguel Fuentes-Cabrera and Bobby Sumpter at ORNL was already successfully ongoing, as manifested by a joint computational project (CNMS2008-016) and a joint publication addressing a chemical modification of the thymine nucleobase (J. Phys. Chem B, published online Oct. 8, 2009).
The second main goal of the visit was to identify future prospective collaborations.

WORK CARRIED OUT DURING THE VISIT

♦ Identification of the most promising chemical modifications of xDNA bases that can induce variations of the electronic levels and the gap exploitable for nano-technological applications, between all the possible substitutions investigated by the group of Miguel Fuentes-Cabrera e coworkers.
The selected stacks are: xA...xA; xA-OH...xA-OH; and xA-CN...xA-CN. The structure of each monomer (xA; xA-OH and xA-CN) was optimized with MP2/6-31G**. The binding energy for the stacked of two bases were computed with MP2/6-31G*, and the changes in the binding energy with the twist angle was also investigated. According to our calculations, all such substitutions increases the binding energy.
♦ Calculation of the electronic properties of the model periodic stacks within the plane-wave pseudopotential DFT framework as implemented in the PWSCF software, on ORNL computational facilities. The applicant has employed the PBE exchange-correlation functional, ultrasoft pseudopotentials and a plane-wave kinetic-energy cutoff of 25 (200) Ryd for the electron wave functions (charge density).
♦ Main Results: The electronic band structure calculations of the periodic stacks for the substituted and un-substituted systems show that even if the present chemical modifications are increasing the

binding energy, they do not involve the π-system of the x-Adenine (in line with what observed by S. E. Wheeler and K. N. Houk, JACS (2008), ***130***, 10854-10855 for substituted benzene rings). The fundamental gap shrinking of the substituted systems, relative to the natural systems, are quite small and practically negligible (see Fig. 1). Furthermore, especially for the rotated (36° deg) xAdenines stacks with both –OH and –CN substitution, the bands become flat, indicating the no semiconductor-like state in the sequence with a rotation angle typical of B-DNA. For this reason the applicant and the host have further planned, during the visit, to perform new calculations at different levels of theory (SAPT, Van der Waals-DF etc) including the dependence on the stacking distances between the monomers in the stacks, and to compare the results with the DFT calculations.

In particular the inclusion of dispersion interactions (Fig. 2 and Fig. 3), calculated for the same periodic stacked structures, leads to very little differences in the observed band structure trends. Furthermore, vdW-DF does seem to underestimate the band gap more than the typical DFT, but the trends hold.

♦A joint publication with staff members at the host institution at ORNL on this topic is currently being finalized.

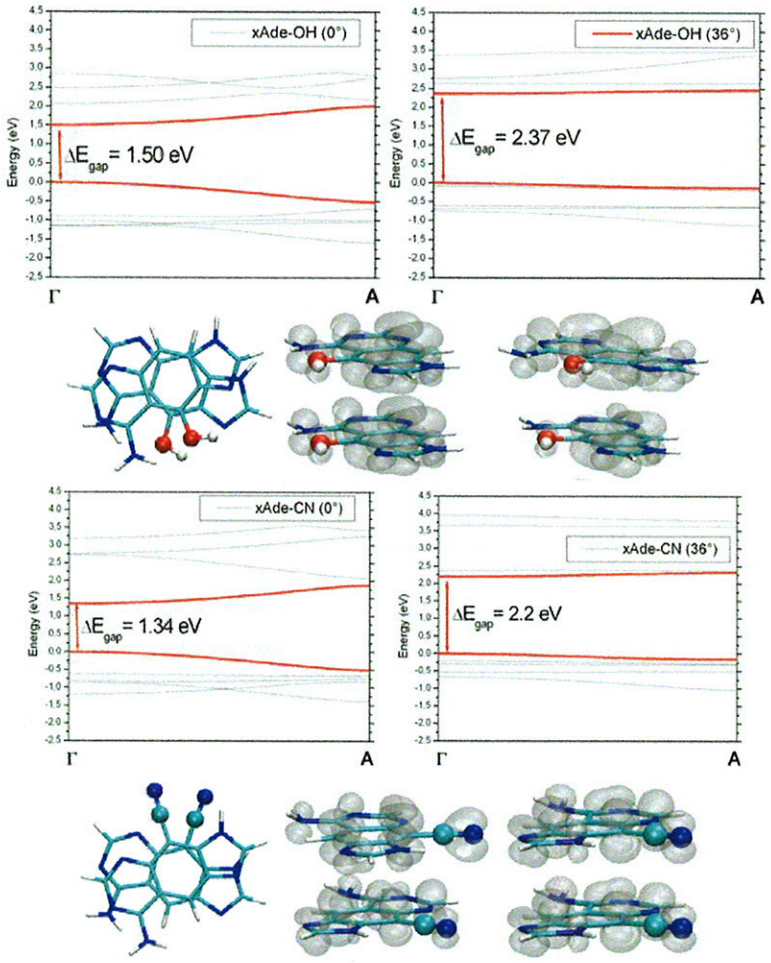

Fig. 1 Periodic stack of non rotated (0° deg) and rotated (by 36° deg) xAdenine with OH- substitution (top panel) and CN-substitution (bottom panel). Band structures, relaxed stacked geometries and HOMO states.

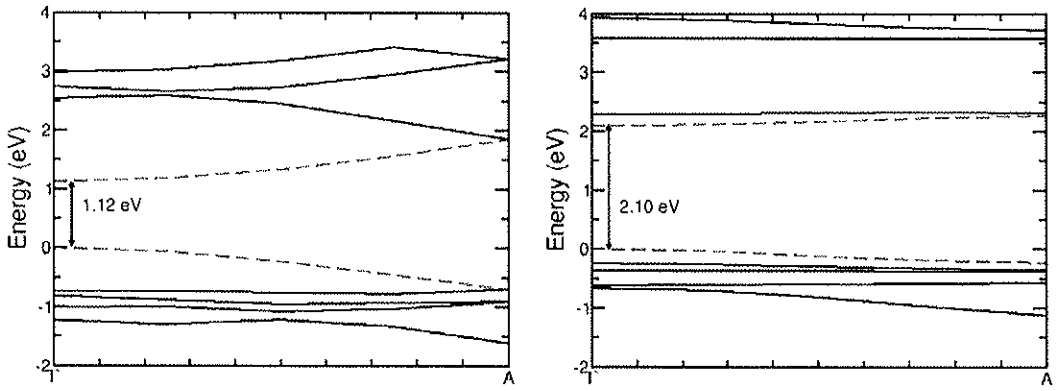

Fig. 1 (left) xAdenine+CN (rotated 0°) and (right) xAdenine+CN (rotated 36°) band structure including VdW

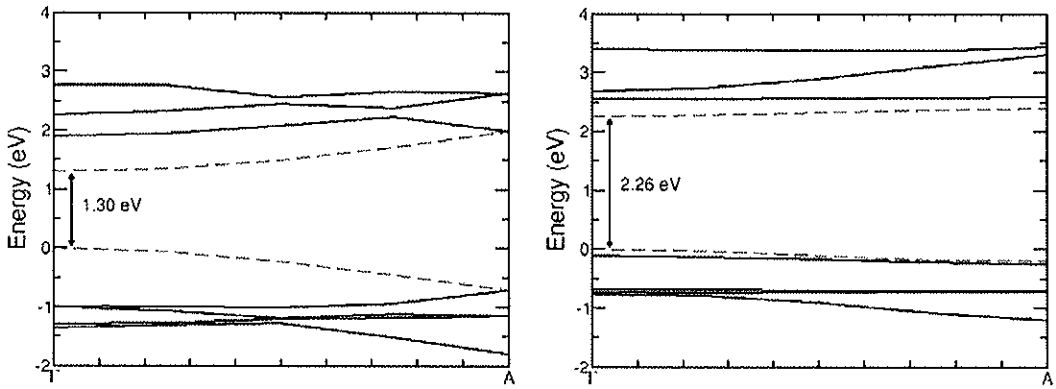

Fig. 2 (left) xAdenine+OH (rotated 0°) and (right) xAdenine+OH (rotated 36°) band structure including VdW

FUTURE COLLABORATION WITH THE HOST INSTITUTION

♦ During the visit, G. Brancolini and R. Di Felice, together with other CNMS staff at ORNL, have discussed a new research proposal to ask for new computing hours at CNMS facilities, to continue along the same research line, by addressing other possible chemical changes and including more extensively the effects of structural fluctuations induced by different environmental conditions. The plan is to continue the collaboration by studying other classes of DNA and xDNA modifications. We have also discussed different strategies, in the frame of novel computational methodologies, to tackle the issue of finding novel derivatives improving the transport and conductivity properties of DNA (xDNA) duplexes.

♦ As a result of the present SHORT-TERM MOBILITY, the applicant (Giorgia Brancolini) and the CNMS staff members (Miguel Fuentes-Cabrera and Bobby Sumpter) have written a Partner Research Proposal titled "Multi-scale modelling of chemically modified DNA sequences for nanotechnology and molecular biology" (for the upcoming next two years) in which we plan to investigate new classes of DNA molecules for some of which new force fields will be developed and made available to the scientific community, as to facilitate future studies in the artificial DNAs.

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..... Modena, 29 Ottobre 2009