Electronic structure of DNA nucleobases and their dinucleotides explored by soft X-ray spectroscopy

Yoshihisa Harada,[1] Tomoyuki Takeuchi,[1] Hiori Kino,[2] Akiko Fukushima,[3] Kaoru Takakura,[4] Kotaro Hieda,[5] Aiko Nakao,[6] Shik Shin,[1,7] Hidetoshi Fukuyama[8]

[1]*RIKEN SPring-8 center, 1-1-1 Kouto Sayo-cho Sayo-gun Hyogo 679-5148, Japan*
[2]*National Institute for Materials Science, 1-2-1 Sengen Tsukuba Ibaraki 305-0047, Japan*
[3]*Photon Factory, 1-1 oho Tsukuba Ibaraki 305-0801, Japan*
[4]*International Christian University, 3-10-2 Osawa Mitaka Tokyo*
[5]*Rikkyo University, 3-34-1 Nishi-Ikebukuro Toshimaku Tokyo 171-8501, Japan*
[6]*RIKEN, 2-1, Hirosawa, Wako-shi, Saitama 351-0198, Japan*
[7]*ISSP, University of Tokyo, 5-1-5 Kashiwanoha Kashiwa Chiba 277-8581, Japan*
[8]*IMR, Tohoku University, 2-1-1 Katahira Aoba-ku Sendai Miyagi 980-8577, Japan*

E-mail; harada@spring8.or.jp

Recently several contradictory experimental results have been reported on the electronic property of DNA, wherein DNA has been claimed to be a wide gap semiconductor to a metal, and even a superconductor [1]. Since the electronic states of DNA near the band gap are determined by a combination of electronic states derived from the nucleobases, ribose rings, phosphates, and counter ions, it is important to understand the origin of the electron migration in DNA with the knowledge of the valence electronic structures of the building blocks of DNA. For this end, soft X-ray spectroscopy provides direct information about the electronic structure, including element and site specificity. Since the nitrogen atom is only included in the nucleobases, we can track changes in the electronic structure of the nucleobases by using N 1s core excitation. Thus we applied N 1s X-ray absorption spectroscopy (XAS), X-ray photoemission spectroscopy (XPS), and X-ray emission spectroscopy (XES) to the nucleobases and their dinucleotides. The XAS and XES spectra reflect unoccupied and occupied partial valence DOS, respectively, where the 'partial' refers to the orbital-selectivity in the core-to-valence optical transition. The N 1s XPS spectra can be used to determine the Fermi level.

Figure 1 shows N 1s XES spectra of single crystal nucleobases, i.e., adenine, guanine, cytosine, and thymine, plotted against binding energy [2]. The arrows indicate the ionization potential of the nucleobases. As expected from recent PES results [3], the guanine base is the site with the lowest binding energy among them. Combined with the XAS and XPS results, we will argue a disruption of the aromatic character of the six-membered ring in the guanine dinucleotide, which leads to an enhanced localization of the π states and may play an important role in the electronic conductivity of DNA.

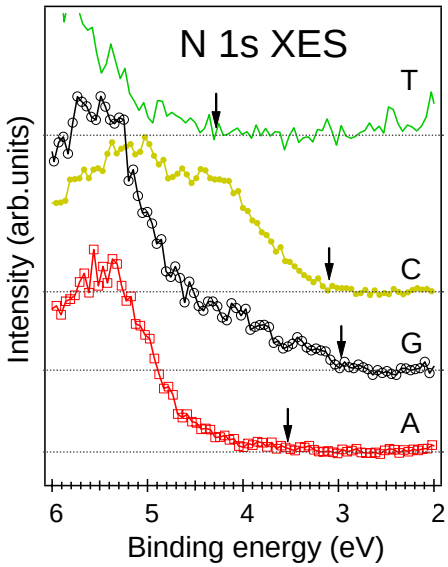

Figure 1: N 1s XES of nucleobases

[1] A review of the experiments can be found in http://mike.zwolak.org/publications/DNA_Electronics.pdf.
[2] Y. Harada *et al.*, J. Phys. Chem: A, **110** (2006) 13227.
[3] X. Yang *et al.*, Proc. Natl. Acad. Sci. USA **44** (2004) 1197.