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# Fluorescence XAFS measurements of DNA film immobilized on organic SAM

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## 1 Introduction

Monochromatic soft X-rays have been used as a probe to control the initial process of DNA damage induction. Fujii *et al.* reported that yields of radiation damage in DNA including strand breaks and oxidative lesions of nucleobases depend strongly on the soft X-ray energy tuned around *K*-edges of DNA constituent atoms, namely carbon (280 eV), nitrogen (400 eV) or oxygen (530 eV). They used the thin layer samples of DNA dropped and dried on an inorganic substrate. The chemical state of the thin layer DNA is substantially different from that in vivo DNA which twines round histone proteins. In our previous study[1], to simulate in vivo DNA, we suggested a new model of the DNA sample using self-assembled monolayer (SAM). The obtained results showed that the DNA molecules were strongly immobilized on the SAM. In this report, to understand the chemical state of immobilized DNA in solution, fluorescence XAFS were measured.

## 2 Experiment

We used mercaptopropyltrimetoxisilane (MPTS) molecules ($HS(CH_2)_3Si(OCH_3)_3$) as an organic SAM on sapphire C-planes. MPTS molecules have thiol group (SH) and silicon alkoxide ($Si(OCH_3)_3$) at the respective terminal sites of the alkyl backbone. Oligonucleotide (OGN) molecules were used as a DNA sample.

Five samples were prepared and showed in Table 1. Sample (a) is an OGN thick film as a reference sample. For sample (b), the OGN molecules were dissolved in 10 mM Tris-HCl solution. Sample (c) was prepared by dropped 100 μM OGN solution, then the surface was washed by supersonic waves. As sample (d) and (e), MPTS molecules were adsorbed on sapphire by immersing the substrate in 10% ethanol solution. Then, 100 μM OGN solution was dropped on the MPTS film. Only sample (d) was dried in air. The samples were measured by NEXAFS (near edge X-ray absorption fine structure).

Table 1: Prepared samples

| **Sample** | |
|---|---|
| **(a)** | Oligonucleotide thick film |
| **(b)** | 100μM oligonucleotide solution |
| **(c)** | Oligonucleotide thin film on sapphire |
| **(d)** | 100μM oligonucleotide/MPTS/Sapphire (dry) |
| **(e)** | 100μM oligonucleotide/MPTS/Sapphire (wet) |

## 3 Results and Discussion

P *K*-edge fluorescence NEXAFS spectra show in Fig.1. Observed peaks (i) and (ii) originate from P 1s to 6e, and to $9a_1$+7e orbital, respectively[2]. The presence of peak (i) indicates $PO_4^{3-}$, thus, phosphoric acid in OGN molecules. Compared with the film and solution sample, for example (a) and (b), the peak energy was not shifted. Moreover, the same results were obtained in the case of the MPTS film existing or not, such as (a) and (d). These results suggest that the chemical state of the phosphoric acid in OGN molecules is stable and is not affected by the ambient environment. Concerning the spectrum of (c), the peak intensity is low than that of other samples. In previous study, we proposed that the OGN molecules are immobilized on the MPTS-SAM through chemical bonds. The sample (c) was prepared by dropped the OGN solution on sapphire surface without MPTS film. Therefore, the peaks were not observed because the OGN molecules were not immobilized on the surface. In summary, it is suggested that the chemical state of phosphorous atoms in OGN molecules immobilized on MPTS film is chemically stable, and the OGN molecules were adsorbed on the MPTS film strongly.

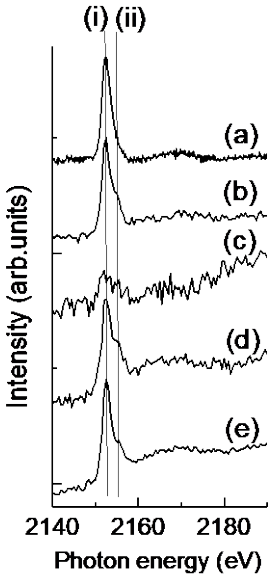


Fig.1: P *K*-edge NEXAFS spectra of OGN samples.

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