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Electron transfer dynamics in 5'-Guanosine monophosphate interfaces probed by core-hole clock method

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Introduction

To aid our understanding the electron transport properties of DNA, it is useful to study interfacial interaction between each nucleotide building block of DNA. In particular, 5'-Guanosin monophosphate (GMP), one of the four nucleotides has received much greater attention than other nucleotides because of unique aggregated structures such as G-quartet formed by self-association of Guanine or related systems and the lowest oxidation potential of the nucleobases. The G-quartet is important for many areas ranging from biology to supermolecular chemistry and nanotechnology[1].

Experimental

Experiments were performed at beamline BL-27A with energy resolution of 0.9 eV around the P *K*-edge using Resonant Auger Spectroscopy (RAS) and X-ray absorption spectroscopy (XAS). GMP disodium salt was obtained from Tokyo Chemical Industry Co., Ltd. (98% purity by LC-analysis). In comparison, a synthesized 10-mer single-stranded polyguanylic acid (polyG) and DNA sodium salt was also used. The as-received powdered samples were placed on conductive carbon tapes or firmly pressed onto indium substrates.

Results and discussion

Partial yields for 2h1e and 2h Auger final states were obtained at each excitation energy from peak areas for spectator and normal Auger, respectively, as shown with the P *K*-edge XAS in Fig. 1. No significant shape differences were observed between GMP and DNA[2], where 2h1e and 2h yield spectra correspond to a localized and delocalized component of partial DOS of t_2* near Fermi energy (E_F), respectively. Some data points of polyG are consistent with GMP as shown in Fig. 1.

The microcrystalline GMP is supposed to be a stack of tetramers (G-quartet) with a helical structure and polyG could also be a similar helical structure based on X-ray diffraction study [3]. Therefore, the similarity of spectral features can be understood by the fact that GMP and polyG crystalline structures mimic DNA.

To compare the previous results of DNA[2], we examined the electron delocalization time (τ_{ED}) of the P 1s core-excited electron to the empty conduction band of t_2* orbitals for GMP using the core-hole clock method[4] . The τ_{ED} for GMP is shown as a function of excitation energy in Fig. 2. The timescales of GMP, and dry and wet DNAs are relatively similar in each other. However, their slopes of curves slightly differ, where solid lines show exponential fits to the measured data. The slopes of curves might have some relation to the tunneling barrier through phosphate groups. The more gradual slope probably corresponds to more delocalized conduction band state. Considering that G-quartet formed by GMP reflects telomeric DNA, it is expected that electron transfer through phosphate groups might occur more easily in telomeric parts compared to ordinary DNA parts.

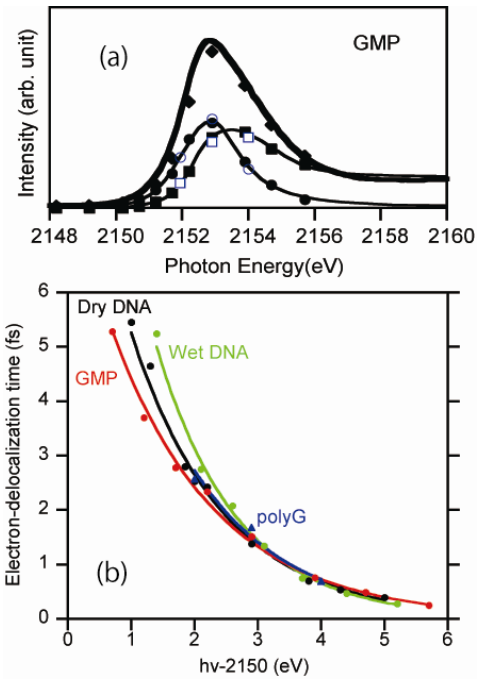

Fig.1 (a) Partial yields for 2h1e (•) and 2h (■) Auger final states for GMP with results of fitting (thin solid lines). The sum of cross sections is shown as ♦, which is similar to XAS (thick solid line). Some data points of polyG are also plotted (blue). (b) Excitation energy dependence of electron-delocalization time for GMP, polyG, and dry and wet DNAs with an exponential fit.

References

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