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Femto- and attosecond electron dynamics in 5_-Guanosine monophosphate interface as probed by resonant Auger spectroscopy†

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To help in our understanding of the electron transport properties of deoxyribonucleic acid (DNA), it is useful to study the interfacial interaction between each nucleotide building block of DNA. Electron transfer properties between phosphate groups in microcrystalline 5_-Guanosin monophosphate (GMP) were probed using energy-dependent resonant Auger spectroscopy. Results show that the phosphate group of GMP forms an extended state along the phosphate directions similar to the case of DNA phosphate backbones. Electron delocalization time of the phosphate groups in GMP is faster than those of DNA, as estimated using the core-hole clock method. This suggests that interface between GMP phosphate groups would have the lowest tunneling barrier among DNA related systems. Although the $\pi - \pi$ coupling of nucleobases is only recognized as charge-transfer pathway in DNA and related systems, another conduction pathway through phosphate groups would be possible.

Keywords: Guanosine monophosphate; DNA; X-ray absorption spectroscopy; resonant Auger spectroscopy; electron transfer; polyguanylic acid

Introduction

The electrical charge transport through deoxyribonucleic acid (DNA) molecule is a key role for understanding recognition, signalling and repair of DNA damage related to the process of cancer and aging[1,2] and for future applications as a conducting molecular wire.[3] To understand charge transport properties at the level of a single molecule, the molecular wire is placed between two nano electrodes. However, chemical interaction between the molecule and the electrode modify the density of state at the Fermi level for the molecule (e.g. Ref. [4] and the reference therein). In this case, the transport properties measured are affected by not only the molecule but also the electrode-molecule-electrode junctions. Actually, the electrical conductivity of DNA is still controversial although a number of direct electron transport measurements of DNA wires have been performed at the single-molecule level (e.g. Ref. [5] and the reference therein). Therefore, spectroscopic characterization of a molecular nature without electrodes is useful for understanding the inherent transport properties.

Recently, we reported the observation of delocalized conduction band along the periodic backbones of genomic DNA using resonant Auger spectroscopy (RAS).[6] To help in our understanding of the electron transport properties of DNA, it is useful to study the interfacial interaction between each nucleotide building block of DNA. In particular, 5_-Guanosin monophosphate (GMP) (Fig. 1), 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.[7] Most measurements specifically assess charge transport through the $\pi - \pi$ coupling of nucleobases in G stacks because sugar and phosphate groups are considered to have wider band gaps than bases. However, when unoccupied electronic states are delocalized along the phosphate direction, another conduction pathway would be possible by doping or related methods.[8]

In this paper, in continuation of the previous DNA work,[6] we present electron transfer properties of phosphate site in disodium GMP microcrystalline powder probed by RAS. In this spectroscopy, we used core-hole lifetime ranging from femtoseconds (10^{-15} s) to attoseconds[9] (10^{-18} s) as a fast internal clock. This is the socalled core-hole-clock method (e.g. Ref. [10] for review), which was originally applied to studies of charge transfer from adsorbed atoms or molecules into substrates. Such a short time period is difficult to analyze using traditional methods like ultrashort pulse laserpump-probe spectroscopy. In a one-dimensional polymeror a condensed matter system, dynamics of an initially localized core excited state (Fig. 2(a)) is interpreted based on two competing decay channels: core-hole decay (e.g. P 1*s* core-hole lifetime is c.a. 1.25 femtoseconds[9]) and core-excited resonant electron delocalization (femto- and attosecond timescale). If the resonantly excited electron exists sufficiently long enough to be localized in the vicinity of a core-hole site during the core-hole decay, the decay process results in final states of two holes with one electron (2h1e), known as ‘spectator Auger’ (Fig. 2(b)). Alternatively, if it delocalizes to the

conduction band prior to the core-hole decay,

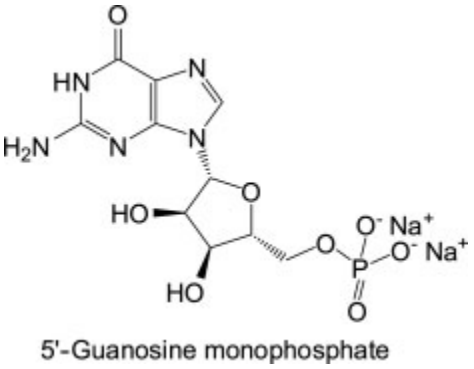

Figure 1. The chemical structure of GMP disodium salt.

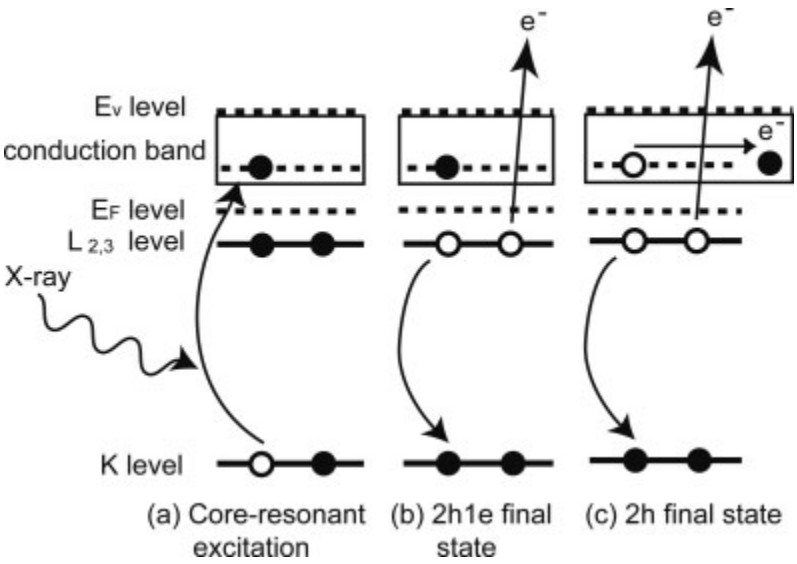

Figure 2. (a) P 1s core electron is excited into an unoccupied state in the conduction band. (b) Spectator Auger final state (2h1e) caused by localization of the electron to the core-hole site. (c) Normal Auger final state (2h) caused by delocalization of the electron to the conduction band coupling to the continuum.

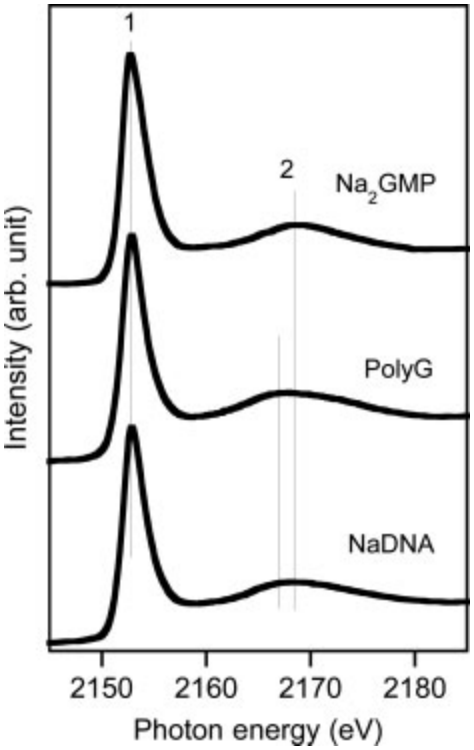

Figure 3. P *K*-edge XAS spectra for GMP, polyG and DNA.

the decay process results in final states of two holes (2h), known as ‘normal Auger’ (Fig. 2(c)). For this scheme, if phosphate sites form a ‘fast’ delocalized conduction band state, an excited electron can delocalize through the phosphate groups before core-hole decay. Consequently, the normal Auger yields are regarded as reflecting the conduction band structure in analogy to metal[11] and semiconductor.[12]

Experimental

Experiments were performed at beamline BL-27A of the Photon Factory, High Energy Accelerator Research Organization (KEK-PF) in Tsukuba. The BL-27A is equipped with an InSb(111) double-crystal monochromator with energy resolution of 0.9 eV around the P *K*-edge. The RAS spectra were measured using a hemispherical analyzer (CLASS-100; Vacuum Science Workshop (VSW)) with pass energy of 44 eV. X-ray absorption spectroscopy (XAS) spectra were measured by monitoring the sample drain current. 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; Tsukuba Oligo Service Co. Ltd) and DNA sodium salt (Acros Organics) was also used. The as received powdered samples were placed on conductive carbon tapes or firmly pressed onto indium substrates.

Results and Discussion

Figure 3 shows the P *K* edge XAS of GMP compared to those of polyG and DNA. Peak 1 can be assigned to P 1*s* → t_{2*} and peak 2 to shape resonance transition based on the previous XAS studies of phosphate compounds.[13] It is noteworthy that P 1*s* → a_{1*} transitions (the lowest unoccupied molecular orbital, LUMO of phosphate group) are forbidden because of the *s* character of these orbitals. The t_{2*} exhibits a strong contribution of both oxygen 2*p* and phosphorus 3sp_3 hybrid orbitals.[13] Although overall spectral features are very similar to each other, the shape resonances are slightly different. The shape resonances of polyG and DNA are shifts to lower energy as producing sugar-phosphate repeating units, which might be related to energy levels in the ground state. Similar phenomena were observed in polythiophene and monomer units.[14] In contrast, almost the same features are observed in the unoccupied states of t_{2*}. The equivalent spectral feature suggests that GMP and polyG form conduction band states through phosphate groups in analogy to DNA,[6] and phosphate ionic states are similar to each other because of different protonation states showing different spectral features.[15] XAS is commonly recognized as reflecting unoccupied partial density of states (DOS), but it can not distinguish localized (core exciton) and delocalized (conduction band) states. Therefore, RAS is applied to GMP to investigate the conduction band state.

Information related to the degree of delocalization of the unoccupied conduction band is obtainable by plotting the spectator (localization) and normal (delocalization) Auger intensities in RAS as a function of the photon energy. A typical P $KL_{2,3}L_{2,3}$ RAS of GMP at the t_{2*} transition is shown in Fig. 4(a), where spectator and normal Auger peaks are observed. The spectator Auger feature is shifted to higher kinetic energy compared to the normal Auger feature because of the screening interaction of a core hole with the localized spectator electron. The spectator shift of GMP is similarto that of DNA[6].

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 XAS in Fig. 4(b). Although there are other possible resonant decay pathways such Femto- and attosecond electron dynamics in

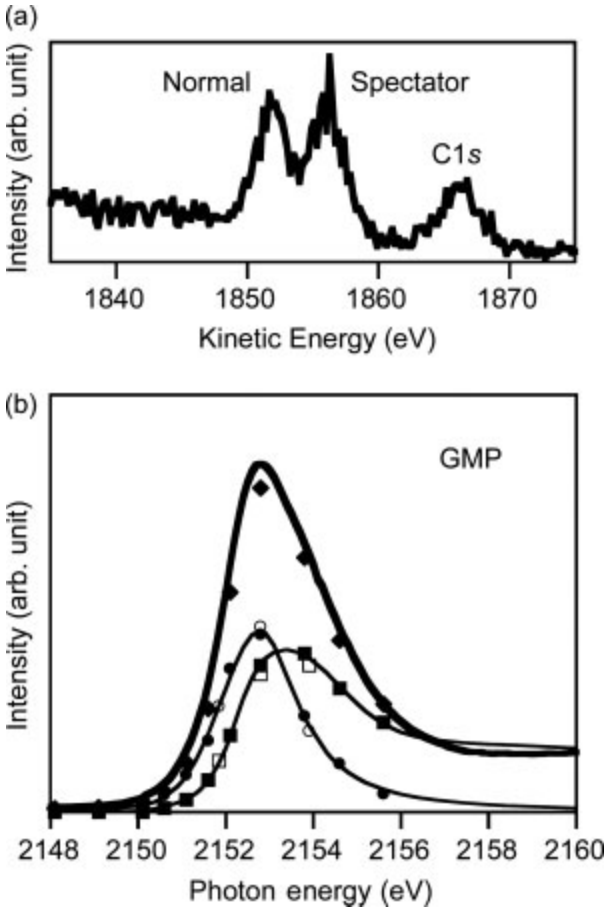

Figure 4. (a) A typical P *KLL* resonant Auger spectrum of GMP at 2152.8 eV. Spectator Auger and normal Auger features are visible. (b) Integrated intensities of spectator (closed circle) and normal (closed square) Auger components for GMP near the P *K*-edge. Results of curve fitting for 2h1e and 2h spectra are shown as thin solid lines. The sum of 2h1e and 2h cross-sections is shown as closed diamonds, which is similar to P1s XAS (thick solid line). Some data points of integrated intensities of spectator (open circle) and normal (open square) Auger components for polyG are also plotted.

as participant Auger, the spectator Auger can be ascribed to the dominant decay pathway because the sum of normal and spectator contributions shows a clear resemblance to the XAS. No significant shape differences were observed between GMP and DNA[6], 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 and also DNA as shown in Fig. 4(b). The microcrystalline GMP used here 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[16]. Therefore, the similarity of spectral features can be understood by the fact that GMP and polyG crystalline structures mimic DNA. Inherently the

phosphate group should have a character of insulator because of its large band gap. However these RAS results suggest that there are conduction electrons through the phosphate groups. Therefore DNA and related systems would be wide-band gap semiconductors by doping or related techniques, likely to diamond.

To compare the previous results of DNA[6], we examined the lectron 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. The relationship between the τ_{ED} and the relative intensity of 2h and 2h1e final states can be described based on previous studies[10] as: $\tau_{ED} = \tau \times (I_{2h1e}/I_{2h})$, where τ is the core-hole lifetime. Therein, I_{2h1e} and I_{2h} respectively represent intensities of spectator and normal Auger components. The P 1*s* core-hole lifetime of 1.25 femtoseconds[9] is used for τ. The τ_{ED}

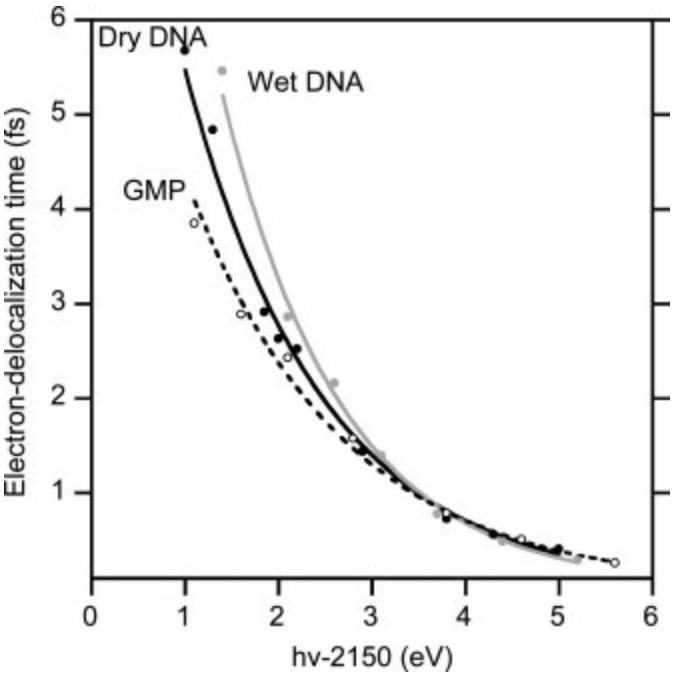

Figure 5. Excitation energy dependence of electron-delocalization time for GMP, and dry and wet DNAs. Each solid line is obtained by an exponential fit.

for GMP is shown as a function of excitation energy in Fig. 5. The τ_{ED} shortens with increasing excitation energy. This energy dependence is expected to result from the tunneling barrier and DOS in the conduction band, based on the previous study.[15] The timescales of GMP and dry and wet DNAs are relatively similar to each other. However, their slopes of curves differ slightly, where solid lines show exponential fits to the measured data. A theoretical approach is necessary to interpret the obtained plots, but 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.

Conclusion

We have observed the electron transfer in GMP molecular interface through phosphate groups using RAS. The conduction band structure (normal Auger yields) of GMP is consistent with those of polyG and DNA. This can be understood by the crystalline structural similarity. Energy dependence of electron transfer time between phosphate groups shows exponential decaying tendency but differs slightly in slopes of their curves. It was found that GMP has the most gradual slope among them. This suggests that interface between GMP phosphate groups would have the lowest tunneling barrier. Although the $\pi - \pi$ coupling of nucleobases is only recognized as charge-transfer pathway in DNA and related systems, another conduction pathway through phosphate groups would be possible. A theoretical and further experimental approach is necessary to interpret the results obtained in more detail.

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