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Photogenerated Hole Mobility in DNA Measured by Time-Resolved Microwave Conductivity

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Charge migration in DNA is currently a subject of intense study[1−6] because of its importance in various applications from functional nanoscale electronic devices[7−9] to long-range detection of DNA damage.[10,11] The regularly ordered array of π-orbitals of nucleobases in the interior of the DNA double helix with a stacking distance of approximately 3.4 Å provides a pathway of charge carriers generated on the π-stack. The efficiency of charge transport along the π-stack is usually characterized in terms of the charge carrier mobility.

There have been many approaches to study the electric conductivity along a DNA strand.[12] Contradictory results have been obtained in these studies, with the conductivity values ranging from approximately 1 to 1×10^{-5} S cm^{-1}. This is due to large differences in the methods and the media used for preparing samples. Recently, it has been possible to measure the mobility of charges along isolated chains of conjugated polymers in solution with time-resolved microwave conductivity (TRMC).[13,14] TRMC allows measurement of the conductivity of photogenerated charge carriers on an isolated molecular chain without an attached electrode. Measurements of charge transport on isolated chains provide unique data on charge transport along molecular wires, which is useful for elucidating the relationship between the molecular structure of conjugated polymers and the electronic conductive properties.

In contrast, it has not yet been possible to measure the mobility of charge carriers along the stacks of base pairs on DNA in solution. It is not possible to carry out TRMC experiments in aqueous solution because the probing microwave is completely absorbed by water due to its high dipole moment. To resolve this problem, in the present work, we examined the mobility of charge carriers in a novel DNA−lipid complex that is soluble in nonpolar solvents.[15] Here, we report the first direct observation of charge transport dynamics using TRMC and transient absorption spectroscopy on the photolysis of an anthraquinone-bound DNA complex.

The duplex oligonucleotide DNA used this study, **1**, was synthesized by Sigma Genosis Biotech Co., Japan.

1

The oligonucleotide was dissolved in 20 mM potassium phosphate (pH 7.0). Annealing of the two strands was accomplished by heating the samples to 90 °C for 5 min and then allowing the samples to cool slowly back to room temperature over a period of 1 h. The DNA−lipid complex was prepared as follows.[15] A 150 μL sample of aqueous solution of DNA **1** ($\sim$500 μM) was mixed with an aqueous solution of cationic dimethyl dipalmitylammonium bromide (2 mM) at room temperature. The precipitated DNA−lipid complex was collected by centrifugation and dried in a vacuum. The obtained DNA−lipid complex was soluble in most hydrophobic organic solvents, such as CCl_4, $CHCl_3$, and dioxane, but not in aqueous media. An anthraquinone sulfate (AQS)-bound DNA−lipid complex was prepared by mixing an aqueous solution of DNA containing 2−4 equiv of AQS to DNA and lipid. Intercalation of AQS in the DNA−lipid complex was confirmed by the appearance of a induced CD band around 325 nm.[16] On the basis of absorption measurements, one AQS molecule intercalated per approximately 10 base pairs of DNA−lipid complex. The melting temperature (T_m) of the lipid−DNA complex in $CHCl_3$ (30 °C) was the same as that in aqueous solution. Transient conductivity and photoinduced absorption changes were measured in an identical geometry using TRMC and transient absorption spectroscopy systems.[17]

Figure 1 shows the CD spectra of the DNA **1**−lipid complex in $CHCl_3$ as a function of temperature. The DNA−lipid complex shows positive Cotton effects at 260 and 275 nm and a negative Cotton effect at 245 nm, similar to native DNA in aqueous solution.[18] This indicates that the DNA−lipid complex forms a double helical B-form structure even in organic solvents. When the temperature was increased, the positive Cotton effects decreased and shifted to longer wavelengths. These changes are completely reversible, as assessed by cooling and reheating of the sample.

Irradiation of the AQS intercalated in the duplex nucleotides causes a charge separation between AQS and an adjacent base, producing an AQS radical anion and a base radical cation (hole). In DNA **1**, a part of the holes escapes from the initial charge-recombination process and is trapped at GGG. Figure 2A shows the transient optical absorption decay at 460−510 nm after laser photolysis of the AQS-bound DNA **1**−lipid complex in CCl_4. We assign the transient species with an absorption maximum at 480 nm (inset of Figure 2A) to the AQS radical anion.[16,19] The subsequent slow decay process (Figure 2A) is due to a charge recombination between the AQS radical anion and GGG$^{\bullet+}$. Change in solvent between $CHCl_3$ and dioxane had little effect on the decay process, suggesting that the solvent is not important as charge migration in this system.

Laser photolysis of AQS-bound DNA **1** in CCl_4 (Figure 2B) caused an increase in conductivity, and subsequent decay on a microsecond time scale was observed.[20] A significant difference in the decay kinetics between the transient absorbance change and the conductivity change was not observed. On the other hand, laser photolysis of CCl_4/anthraquinone solution without DNA (Figure 2B) caused a small change in conductivity, due to the low mobility of the anthraquinone radical anion. Therefore, it can be concluded that the changes in the conductivity of the AQS−DNA complex originate from positive charge carriers in the DNA bases. On the basis of the current data, we calculated the mobility of holes in DNA **1** as 5×10^{-3} cm^2/Vs. This is comparable to the values for conjugated polymers (1.0×10^{-3} to 1.0 cm^2/Vs),[12,13] but is much

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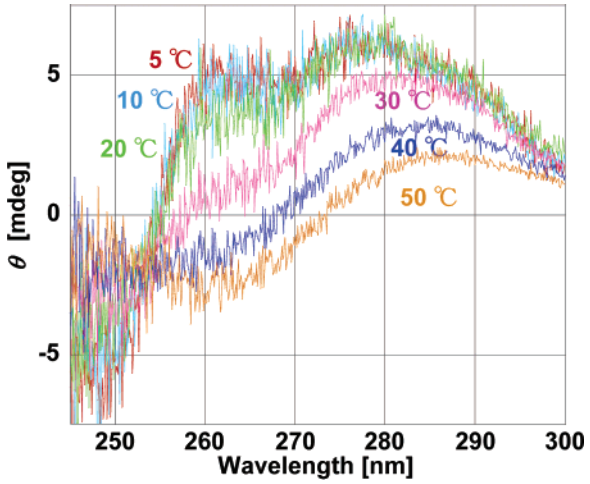

Figure 1. Temperature-dependent changes in CD spectra of DNA−lipid complexes in $CHCl_3$.

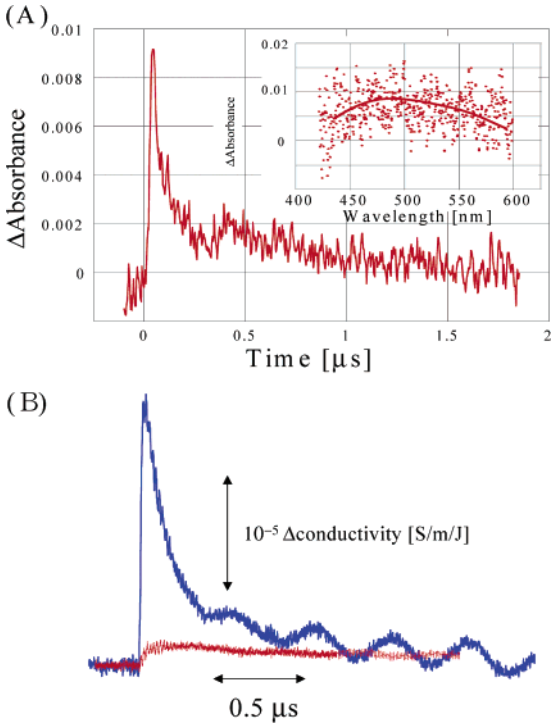

Figure 2. (A) Decay at 460−510 nm ranges of AQS-bound DNA **1**−lipid in CCl_4 measured by transient absorption spectroscopy on 355 nm excitation. The inset shows transient optical absorption at the end of the pulse. (B) Laser power-normalized transient conductivity of AQS-bound DNA **1** (blue line) and anthraquinone in CCl_4 (red line) measured by TRMC.

lower than that theoretically predicted for an ideally ordered poly(G)−poly(C) duplex (10 cm^2/Vs).[21] The observed conductivity may result from the intrinsic mobility of the hole trapped at the GGG site in DNA **1**. The difference in the carrier mobility and dynamics of different oligonucleotides is of particular interest because they may be drastically affected by the interaction fields induced by base pairing and base stacking.

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(17) The resonant frequency and the microwave power were ~9.1 GHz and 3 mW, respectively. The THG (355 nm) light pulse from a Nd:YAG laser (5−8 ns pulse duration) was used as an excitation source. The photon density of the laser was approximately 1.5×10^{16} photons/cm^2. The probe light from a Xe lamp was guided into a high-dynamic-range streak camera (Hamamatsu C7700) which collects a two-dimensional image of the spectrum profiles of light intensity.
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(20) A change in the conductivity of the medium resulting from mobile charge carriers can be detected as a change in the power level of the microwave. The transient conductivity ($\Delta\sigma$) is related to the reflected microwave power ($\Delta P_r/P_r$) and the sum of mobilities of charge carriers via $\langle\Delta\sigma\rangle = 1/A \cdot \Delta P_r/P_r$ and $\Delta\sigma = N \times e \sum\mu\phi$, where A, N, e, ϕ, and $\sum\mu$ are the sensitivity factor, the number of absorbed photons per unit volume, elementary charge of an electron, quantum efficiency of photocarrier generation, and the sum of mobilities for carriers, respectively.
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