Communications to the Editor

Anisotropic Electric Conductivity in an Aligned DNA Cast Film

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Deoxyribonucleic acids (DNAs) are important as a source of biological information depending on their base sequences. DNA is also interesting as a molecular material that shows a long rod-like duplex structure with base-pair (bp) stacking: the base separation is 3.4 Å while the diameter of the duplex is about 20 Å.[1] It therefore appears to be a good candidate for one-dimensional energy transfer and conduction along the π-electron clouds of stacked bases. Macroscopic electric conductivity has been studied by using fibrous gels in which duplex DNAs are randomly oriented.[2−4] Photoinduced electron transfer between redox dye molecules intercalated in DNA molecules has been studied in homogeneous aqueous solution.[5−7] These reports encouraged us to prepare an aligned DNA film as an anisotropic conductive film, in which counter Na^+ cations were exchanged completely to cationic amphiphiles.[8]

The aligned DNA film was prepared as follows.[8,9] An aqueous solution of DNA from Salmon testes (average MW 1.3×10^6, ca. 2000 bp) was mixed with an aqueous solution of a cationic amphiphile, *N*,*N*,*N*-trimethyl-*N*-(3,6,9,12-tetraoxadocosyl)ammonium bromide.[8] The precipitated DNA−lipid polyion complex (1:1 ratio of phosphate anion to cationic amphiphile) was collected and solubilized in chloroform/ethanol (4:1 v/v). The solution (40 mg mL^{-1}, 4 wt %) was cast on a Teflon plate, and the solvent was evaporated slowly under saturated solvent vapor at room temperature. The obtained self-standing film (ca. 60 μm thick) was transparent, flexibly strong, and water-insoluble. The DNA film could be stretched 2−3 times in length by hand at room temperature. From X-ray diffraction experiments and polarized absorption spectra, DNA strands were confirmed to be aligned with a distance of 41 Å along the stretching direction as schematically shown in Figure 1.[8,9] The distance between stacked base-pairs of DNAs in the film was 3.4 Å, similar to native DNA stacking in the aqueous solution.

The stretched DNA film (20×10 mm, thickness 30 ± 5 μm) was put on a comb-shaped electrode plate as shown in Figure 2.[10] The dc conductivity was measured using an ammeter (R8340A, Advantest, Co., Tokyo) at 25 °C in ambient atmosphere or in an evacuated bottle at 0.1 mmHg. Typical results are shown in Figure 2. When the stretched DNA film was put on the comb-shaped electrode with the DNA strand axis aligned perpendicular to the two Au electrodes, a large ohmic current (0−4.1 μA) was observed that increased linearly with increasing applied voltage up to 0.1 V. On the contrary, when the film was placed with DNA strands aligned parallel to the two electrodes, electric current was hardly observed even at a voltage of 0.1 V (less than 0.08 nA). When the unstretched film was employed, a small current

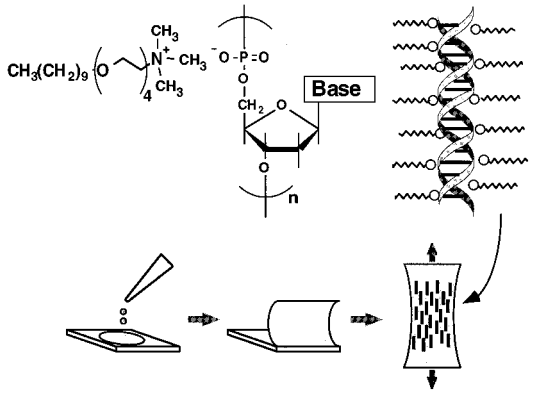

Figure 1. Schematic illustration of a flexible, aligned DNA film prepared from casting organic-soluble DNA−lipid complexes with subsequent uniaxial stretching.

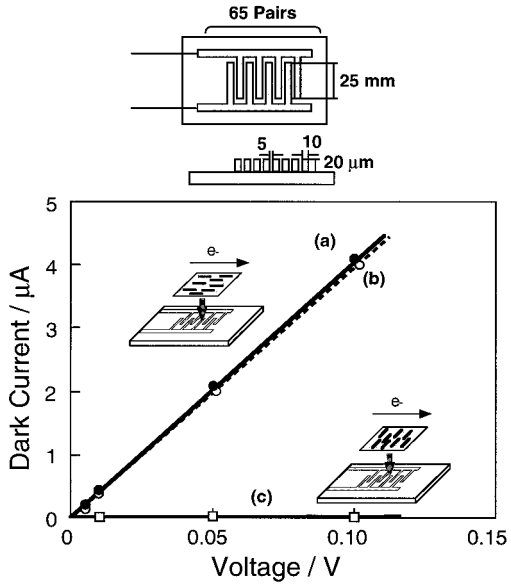

Figure 2. Dark currents for aligned DNA films (20×10 mm, thickness 30 ± 5 μm) on comb-type electrodes at 25 °C. (a) DNA strands in the film places perpendicular to the two electrodes and measured in atmosphere, (b) the same film in (a) measured in a vacuum at 0.1 mmHg, and (c) DNA strands in the film placed parallel to the two electrodes both in a vacuum and in atmosphere.

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(1) Saenger, W. *Principles of Nucleic Acid Structure*; Springer-Verlag: Berlin, 1987.
(2) Lecompte, M. F.; Muller, D.; Josefowicz, M. *Biopolymers* **1972**, *11*, 2563−2575.
(3) Magan, J. D.; Blau, W.; Croke, D. T.; McConnell, D. J.; Kelly, J. M. *Chem. Phys. Lett.* **1987**, 489.
(4) Bakhshi, A. K. *Prog. Biophys. Mol. Biol.* **1994**, *61*, 187−253.
(5) Kumar, C. V.; Barton, J. K.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 5518−5523.
(6) Fromherz, P.; Rieger, B. *J. Am. Chem. Soc.* **1986**, *108*, 5361−5362.
(7) Murphy, C. J.; Arkin, M. R.; Jenkins, Y.; Ghatlia, N. D.; Bossmann, S. H.; Turro, N. J.; Barton, J. K. *Science* **1993**, *262*, 1025−1029.
(8) Tanaka, K.; Okahata, Y. *J. Am. Chem. Soc.* **1996**, *118*, 10679−10683.
(9) Okahata, Y.; Tanaka, K. *Thin Solid Films* **1996**, *284/285*, 6−8.

(10) Contact between the film and the electrode is important to obtain the reproducible results and was performed as followed. The electrode surface was wet with chloroform vapor, and the film was immediately pressed on the electrode.

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was observed ($1 \pm 0.5\ \mu$A at 0.1 V) which was not reproducible. When these experiments were carried out in a vacuum at 0.1 mmHg for 24 h, similar small currents were observed. This means that the water molecules that are hydrating the DNA phosphate groups do not play an important role in the conductivity. When the DNA−lipid film was prepared from a single strand poly(dA), the currents were hardly observed. These results suggest that electric currents may pass through stacked base-pairs of the aligned DNA strands in the film, and phosphate anions or cationic lipids are not important as electron carriers.

Conductivity was calculated to be 5.6×10^{-5} and 10^{-9} S cm^{-1} for current flow parallel and perpendicular to the aligned DNA strands, respectively. Unstretched (as cast) DNA films (DNA strands aligned randomly in the film plane) had conductivity of $10^{-7}-10^{-8}$ S cm^{-1}. Conductivity of conventional polymers such as polyethylene film is observed to be ca. 10^{-10} S cm^{-1} in this condition.[11] Thus, conductivity along the DNA strands increased from 10^2 to 10^4 times by orientation of the film. Conductivity of 10^{-5} S cm^{-1} in the aligned DNA flexible film is reasonable compared with other fragile conventional conductive polymers such as polyacetylene and polyphenylene ($10^{-3}-10^{-1}$ S cm^{-1} without dopants).[11]

Barton and other workers reported that photoinduced electron transfer between donors and acceptors intercalated into DNA strands could be observed in homogeneous aqueous solution.[5−7] We could also observe anisotropic photoinduced electron transfer mediated by intercalated dye molecules through aligned DNA strands in the film. When the aligned DNA film (20×10 mm, $30 \pm 5\ \mu$m thickness) was soaked in an aqueous solution (10^{-3} M) of acridine orange (AO, $\lambda_{max} = 440$ nm) for a day at room temperature, the transparent DNA film turned orange (470 nm) and the aqueous solution became colorless. Adsorbed dye molecules have been confirmed from polarized absorption spectra to be intercalated between base-pairs and to be aligned perpendicularly to DNA strands in the film.[8] Intercalated dyes could not be readily removed from the film after soaking and washing with water for a day. One AO molecule was calculated from absorption measurements of these films to intercalate per ca. 10 base-pairs.

After the film was dried completely in a vacuum for several days, photocurrent was observed using the same electrode setup shown in Figure 2, with pulsed irradiation of light above 380 nm using a 150 W xenon lamp (Hamamatsu Photonics, Co.). As shown in Figure 3, a large ohmic photocurrent was observed when DNA strands were aligned perpendicular, but not parallel, to the two electrodes. Photocurrents increased linearly ($0-0.22\ \mu$A) with increasing applied voltage up to 0.1 V. This photocurrent was reproducible through at least 10 continuous experiments. Dark currents along the AO-intercalated DNA strands ($20\ \mu$A at 0.1 V) were 5 times larger than that of the DNA film without intercalators ($4\ \mu$A at 0.1 V). Thus, the total current ($20 + 0.2\ \mu$A at 0.1V) increased by about 1% using photoirradiation. When

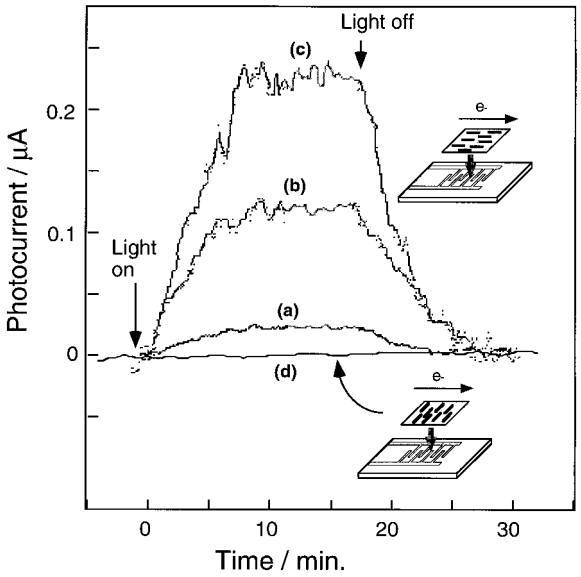

Figure 3. Photoinduced currents for aligned DNA films (20×10 mm, thickness: $30 \pm 5\ \mu$m) in which one acridine orange intercalates per ca. 10 base-pairs. (a) At 0.01 V, (b) 0.05 V, and (c) 0.1 V applied voltage on comb electrodes with DNA strands aligned perpendicular to the two electrodes. (d) DNA strands in the film placed parallel to the two electrodes at 0.1 V. Pulsed light above 380 nm was irradiated from a 150 W xenon lamp at 25 °C.

the unstretched film was employed, both dark- and photocurrents were hardly affected by the AO intercalation. When the DNA−lipid film was prepared from a single strand poly(dA) and soaked in the aqueous solution of AO, dyes did not intercalate (adsorb) into the film and the resulting photocurrent was hardly detectable. These results indicate that photocurrents pass through stacked base-pairs of the aligned DNA strands in the film.[12] Photoinduced current along the DNA strand was calculated to be $7\ \mu$A cm^{-2}, which is fairly large compared to $0.5-1\ \mu$A for fullerene-containing conventional polymer films.[12]

Photocurrents showed a relatively slow rise and decay as seen in Figure 3. Although ohmic heating or other thermal effects should be considered, temperatures measured at the film surface were constant (25 ± 1 °C) during the experiment due to the pulse photoirradiation with adequate cooling. Since it is difficult to precisely change film temperatures during photo and dark experiments, we are not able to explain the slow response of photocurrent.

In summary, we have observed both dark and photoinduced one-dimensional currents along DNA strands aligned in flexible cast DNA films. Detailed conductivity studies including temperature effects are currently under investigation in our laboratory.

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(11) Skotheim, T. A. *Handbook of Conductive Polymers*; Marcel Dekker: New York, 1986.

(12) Bensasson, R. V.; Garaud, J.-L.; Leach, S. L.; Miquel, G.; Seta, P. *Chem. Phys. Lett.* **1993**, *210*, 141.