Reversible Change in Optical Rotation by Phtochromism of Diarylethenes in the Stretched DNA–Quaternary Ammonium Ion Complex Films

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Transparent stretched films of DNA–dimethyldioctadecylammonium ion complex incorporating a photochromic diarylethene exhibited large change in optical rotation by its photochromic reactions. As the stretched films at the photostationary state of UV-irradiation showed the dichroism, it was suggested that the diarylethene molecules are partly intercalated between the DNA base pairs.

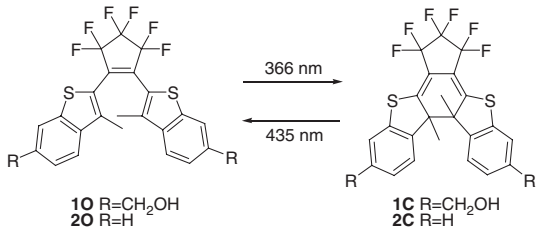
Thermally irreversible photochromic compounds can be applied to photon-mode rewritable optical memory media. Recent development of thermally irreversible photochromic compounds[1] made them close to the application. One of the unresolved problems is how to read the recorded data using light without destroying them. Although several nondestructive read-out methods have been proposed thus far,[2] we believe that to use the change in optical rotation by photoirradiation[3] is one of the most promising methods.

In order to generate changes in optical rotation by photochromic reactions, a photochromic compound should be chiral-non-racemic or should be placed in a chiral environment. Although polypeptides have frequently been used as the chiral media for photochromic reactions both in solution and in films,[4] DNAs have rarely been used as the chiral environment for photochromic compounds, because the fabrication of DNAs into films has been quite difficult. Recently, Okahata et al. succeeded in replacing the sodium cation of the phosphate moiety with quaternary ammonium ion with one or two long alkyl chains.[5] It was found that DNA–quaternary ammonium ion complex (DNA–QAIC) is soluble in organic solvents, and the solution gives transparent and sturdy films after evaporation of the solvent. Furthermore, the film can be stretched mechanically in one direction, so that the DNA strands align in the stretched direction.[5]

As DNAs are known to incorporate rather flat aromatic dyes between the base pairs, we wished to prepare the DNA–QAIC film intercalated by photochromic diarylethenes, in relation to inducing the change in chiroptical properties by photochromic reactions. We here report that **1** showed a remarkably large reversible change of optical rotation in DNA–QAIC films upon alternative irradiation of UV and visible lights among the diarylethenes examined.

Synthesis of 1,2-bis(6-hydroxymethyl-3-methyl-2-benzothienyl)perfluorocylcopentene (**1**) was carried out with the standard procedures reported,[6] and the details will be reported elsewhere. Photochromic reaction of **1** occurs between the colorless **1O** and the orange **1C** as shown in Scheme 1.

DNA used (Nippon Chemical Feed Co., Ltd.) was obtained from salmon milt. The average molecular weight was 6×10^6. Exchange of the cation was done as reported,[5] using dimethyldioctadecylammonium chloride. Although the solubility of DNA–QAIC in organic solvents was poor, it was dissolved in warm chloroform with rigorous stirring. The O-form of **1** was incorporated in DNA–QAIC (base pair:**1** = 100:8.1)[5b] by mixing the chloroform solutions of DNA–QAIC and diarylethene with continuous stirring. A film was obtained by pouring the solution into a flat Petri dish or a Teflon Petri dish, followed by evaporation of the solvent at room temperature. The film thus obtained was stretched to three- to four-fold in length in the stretching direction while the film was exposed to steam.



Scheme 1. Photochromism of diarylethenes **1** and **2**.

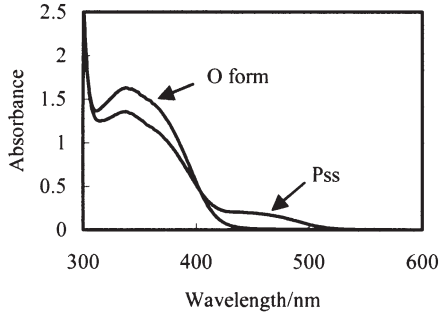


Figure 1. Absorption spectral change of **1** in stretched DNA–QAIC film. **1**: 4.37×10^{-2} mol dm^{-3}, 32 μm thick.

Irradiation of 366-nm light to the stretched colorless films containing **1O** brought about the orange color, indicating the production of the C-form. Irradiation of 435 nm light to the colored film reproduced the colorless film, showing the photochromic reaction occurred in the DNA–QAIC film. Spectral change of **1** in the stretched film upon photoirradiation is shown in Figure 1. By using the molar absorption coefficient in solution

($8500\,mol^{-1}dm^3cm^{-1}$ in toluene at 445 nm (λ_{max}), conversion 92%), the conversion ratio to the C-form in the stretched films were calculated to be ca. 16% ($4.4–5.7 \times 10^{-2}$ mol dm^{-3}, film thickness 43–37 μm).

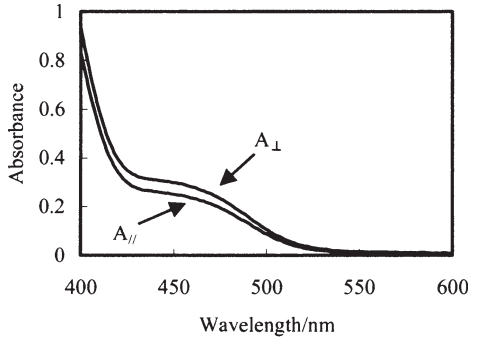


Figure 2. Polarized absorption spectra of **1** in stretched DNA–QAIC film. **1**: 4.37×10^{-2} mol dm^{-3}, 36 μm thick.

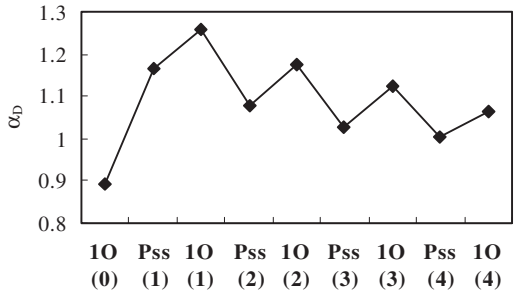


Figure 3. Change in net optical rotation (α_D) at 589 nm in stretched DNA–QAIC film containing **1**. **1**: 4.27×10^{-2} mol dm^{-3}, 37 μm thick.

The polarized absorption spectra of the stretched film containing **1** as its photostationary state (pss) of 366 nm light irradiation on **1O** showed that the absorbance of the visible region when the polarized light is perpendicular to the stretched direction is slightly larger than when the polarization is parallel to the stretched direction (Figure 2; $A_\perp/A_\parallel$ at 445 nm = 1.19). This means that the long axis of **1C** molecule is lying rather perpendicular to the stretched direction, i.e., parallel to the base pairs, because the DNA strands are known to align in the stretched direction.[5] Because of the two angular methyl groups, the whole molecule of **1C** cannot completely be included between the base pairs. Therefore it is likely that a part of **1C** molecule, probably one of the aromatic moieties, is intercalating between the DNA–QAIC base pairs.

The change in optical rotation was then examined. Iterative irradiation of 366 nm (15 min) and 435 nm (8 min) to the stretched film caused alternative change of optical rotation as shown in Figure 3. Except the first measurement of the film just after stretched, the optical rotation changed reversibly, though the magnitude of the change became smaller by iteration. As the DNA strands align in unidirectional mode, the bulk nature of the stretched film resembles to the cholesteric liquid crystal, with the helical arrangement of the DNA main chain and the long alkyl chains of the surrounding ammonium ions. It has been reported that the poly(γ-benzy L-glutamate) films, known to take cholesteric liquid crystalline state, containing spiropyran changed the optical rotation by the photochromism of the spiropyran.[7] The reason of the change of the optical rotation was attributed to the interaction of the colored form with the chiral liquid-crystalline-like ordered structure. Indeed, an induced positive Cotton effect ($\Delta(\Delta\varepsilon)$ 2.6 mol^{-1} dm^3 cm^{-1} at λ_{max} 447 nm) was observed for the same film containing **1**, used to take the absorption spectra (Figure 1).

This phenomenon is general to the diarylethenes. For example, a stretched DNA–QAIC film containing **2** (1.73×10^{-2} mol dm^{-3}, thickness 39 μm) showed similar dichroism and similar change in optical rotation by UV and visible light irradiation. However, the magnitude of change was as small as 0.02° or so. The change strongly depends on the structure.

In conclusion, a large change in optical rotation was achieved by intercalating a diarylethene **1** between the DNA–QAIC base pairs. This phenomenon can be applied to the non-destructive read-out of the optical memory using diarylethenes.

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