Preparation and Photochromic Properties of Powder and Films of DNA–Dodecyltrimethylammonium Ion Complex Containing Spiropyran Derivatives

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Two thermally reversible photochromic spiropyrans, 1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] **1** and 3′,3′-dimethyl-6-nitro-1-(3-sulfopropyl)spiro[2*H*-1-benzopyran-2,2′-indoline] triethylamine salt **2**, were incorporated in powder and films of an organic-solvent-soluble DNA–dodecyltrimethylammonium ion complex. The powder and the films showed thermally reversible photochromism. The spiropyrans in the powder were considered to be intercalated into the DNA base pairs because: 1) they were thoroughly washed to remove weakly attaching molecules and 2) the color of the powder was different from either of the closed or open forms of the spiropyran, whereas spiropyrans doped in the films behaved as in the polar organic solvents, so that the film was a mixture of spiropyran and the DNA–dodecyltrimethylammonium ion complex.

DNAs are helical organic molecules composed of two polynucleotides that most of the living species on earth possess. The hydrogen bonds between the sets of nucleic acid bases, adenine (A) and thymine (T), and guanine (G) and cytosine (C), form the backbone of the helical structure of DNA.[1] The pile of base pairs, stabilized by π–π stacking, is arranged like shelves, and the mean distance of the neighboring base pairs is 0.34 nm. Flat molecules can therefore be incorporated between the base pairs.

Salmon milt is known to contain much DNA, which is easily obtained in large amounts. Because DNA can incorporate various hydrophobic organic molecules, the development of an effective use of DNA as an advanced functional natural polymer is quite important. For instance, efforts towards the development of functional films, such as dye-doped films,[2] fluorescent-dye-doped films,[3] polarized films,[4] and electron conducting films,[5] appeared after a recent report of Okahata and coworkers on the development of water-insoluble, organic-solvent-soluble DNA–quaternar ammonium ion complex (DNA–QAIC) films.[6] DNA–QAIC has many advantageous features over raw DNA. It is soluble in organic solvents, it can be manipulated into a DNA-ordered film by stretching, and it is mechanically strong, yet it can still intercalate organic molecules.

There are several ways to let flat organic molecules, like the aromatic dyes, become settled between the DNA–QAIC base pairs. Soak the DNA–QAIC film in an aqueous solution of a dye for a long time (e.g., 1 d) at room temperature;[6] thoroughly mix a suspension of DNA–QAIC powder in water and a solution of dye in water-immiscible organic solvent, collect the solid DNA–QAIC incorporating the dye, wash it thoroughly, then use the casting method;[7] mix the organic solution of DNA–QAIC and a dye thoroughly followed by the casting method.[2,8]

"Photochromism" is defined as "a reversible transformation of a single chemical species being induced in one or both directions by electromagnetic radiation between two states having different distinguishable absorption spectra."[9] Many photochromic compounds such as azobenzenes, spiropyrans, spirooxazines, fulgides, and diarylethenes have been known so far, and a great amount of effort to improve their reactivity or fatigue resistivity has been devoted to date.[10]

It would be necessary to prepare a photochromic film when photochromic compounds are to be applied to optical devices, such as memories or switches. For this purpose, photochromic polymer films can be prepared by casting or spin-coating a solution of a mixture of polymer and a photochromic compound. Other methods to prepare photochromic films are: 1) introducing photochromic species into the main chain or side chain of polymers[11] or 2) preparing a film of an amorphous photochromic compound.[12] If photochromic dyes can be incorporated into the film with a certain amount, then the film can be made thinner, lighter, and smaller. For this reason, DNA–QAIC is one of the potential candidates to be applied to the construction of optoelectronic as well as photoswitching devices.[2]

As related research, the combination of photochromic compounds and DNA, to control the reproduction of DNA by photoirradiation, have recently been reported by Komiyama and the co-workers.[13,14] However, these are not overlapping with our research goal. Our intention is not to control the function

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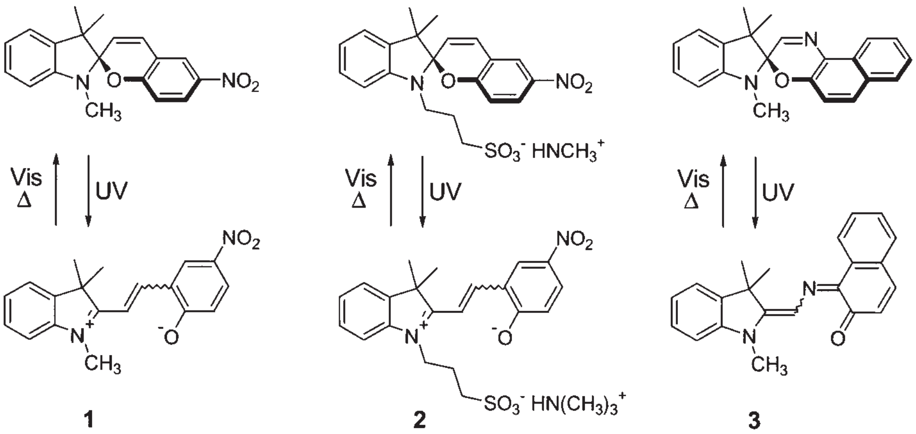


Scheme 1. Spiropyrane derivatives used in this study.

of DNA, itself, but to utilize DNA as the advanced matrix of functional materials. The combination of photochromic dyes and a polyion complex, such as to control the thermal isomerization rate of a spiropyran by the temperature of the system,[15] and to control the aggregate formation by the structure of the photochromic spiropyrans,[16] has also been reported so far. Different from these studies, we wish to use DNA–QAIC by taking advantage of its easy preparation with a simple procedure to modify DNA amply supplied from nature, a broad range of functional groups to be modified, facile biodegradablility including that of quaternary ammonium salt,[17] transparency of the film, capability of incorporating various organic molecules with a certain amount, ordered structure, helical chirality, and so on.

As the first step of such research, we carried out the incorporation of one of the representatives of photochromic compounds, spiropyrans, to see how photochromic dyes act in DNA–QAIC. Although the preparation of DNA–QAIC film containing photochromic dyes was previously suggested,[2] no publications dealing with the preparation and photochromism of DNA–QAIC containing photochromic dyes has yet appeared.[18,19] In this article, our research results on the preparation and photochromic properties of DNA–QAIC powder and films doped with spiropyrans **1** or **2** and a spirooxazine **3** (Scheme 1) are described.

Results and Discussion

Preparation of DNA–QAIC Powder Containing Spiropyran.[7] A powder of DNA–QAIC containing a spiropyran derivative was prepared by mixing DNA–QAIC powder dispersed in water and photochromic spiropyran **1** or **2** dissolved in chloroform until they formed precipitates. After collecting the precipitates by vacuum filtration, they were washed with water and chloroform successively and thoroughly, and the thus-obtained powder was either freeze-dried or vacuum-dried in a desiccator, to yield a powder of the DNA–QAIC–spiropyran composite.

Preparation of DNA–QAIC Films Containing Spiropyran Derivatives. Spiropyran-containing DNA–QAIC films were prepared by drying an ethanol solution containing both DNA–QAIC and the spiropyran derivative (the ratio of the spiropyran derivatives to the base pairs of DNA–QAIC was varied from 0.1 to 0.5[20]) poured into a flat glass Petri dish (diameter 2.5 cm) to afford a transparent film. The thickness of the film was adjusted to be about 20 μm. For control experiments, similar films of polystyrene containing a spiropyran derivative were prepared by a similar casting method, using chloroform as the solvent.

Photochromism of DNA–QAIC Powder Containing a Spiropyran Derivative. The DNA–QAIC, itself, is colorless or slightly yellow, while the powder containing spiropyran is slightly colored with a different color from its open merocyanine form, depending on the kind of spiropyran introduced. Namely, DNA–QAIC containing **1** is yellow, while DNA–QAIC containing **2** is ocher. The irradiation of 366-nm light to the powder for 5–10 min changed the color drastically. The changes in the color of the powder of DNA–QAIC containing spiropyrans **1** or **2** are shown in Fig. 1. From independent experiments, it was confirmed that the powders of **1** and **2**, themselves, not incorporated in DNA–QAIC, did not change their colors upon irradiation of 366-nm light at room temperature. Therefore, the powder obtained from DNA–QAIC and the spiropyran is not just their mixture, but the photochromic molecules are dispersed in DNA–QAIC, and the molecules have sufficient volume to change their structures by photoirradiation. Since the powder was thoroughly washed with water and

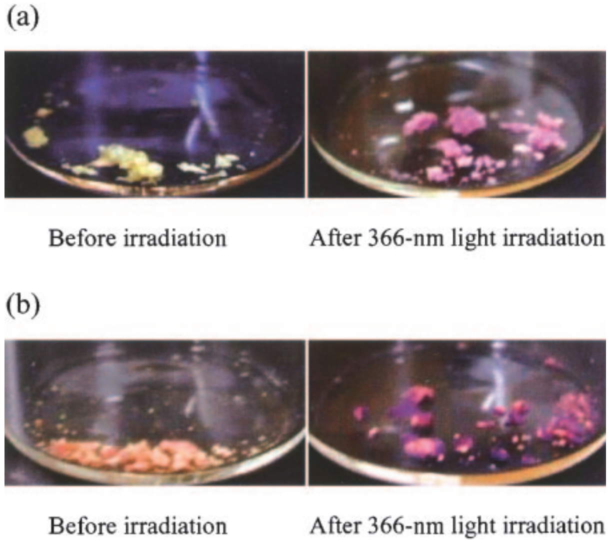


Fig. 1. DNA–QAIC powder. (a) Spiropyran **1**. (b) Spiropyran **2**.

chloroform, spiropyran molecules, which were not strongly attached to the DNA–QAIC, were removed. Therefore, the spiropyran molecules were supposed to be intercalating into DNA–QAIC. Judging from the shape and size of the spiropyran molecule and the width of the DNA shelves, it is natural to estimate that DNA holds the spiropyran molecule with a flat benzopyran moiety rather than the indoline moiety possessing a geminal dimethyl group, or accepting the whole molecule.

Photochromism of DNA–QAIC Films Containing a Spiropyran Derivative. The DNA–QAIC film containing spiropyran is slightly colored with the color of the corresponding merocyanine form, indicating that a part of the spiropyran is in the open colored form. It is in contrast to the powder DNA–QAIC containing a spiropyran. For example, a DNA–QAIC film containing **1** was slightly red-purple. The irradiation of 366-nm light to the film deepened the red color significantly. When the strongly red-purple-colored film was kept at room temperature, the color faded gradually, and the color returned almost to the initial absorbance after 1 d. The lifetime of the colored form of **1** was calculated to be 2.2 h by neglecting the coloration rate constant. The change in the absorption spectra of DNA–QAIC film containing **1** is shown, together with the change in the spectra of **1** in polystyrene film, in Fig. 2.

Different from the DNA–QAIC powder, the small portion of the spiropyran in the DNA–QAIC film existed as the colored form. Because the powder containing spiropyran was washed thoroughly, the spiropyran molecules in the powder were considered to be intercalating. On the other hand, because the DNA–QAIC films were prepared from the ethanol solution containing both DNA–QAIC and spiropyran by evaporation, spiropyran molecules can stay in ethanol, which is a good solvent for spiropyrans, until the last moment of drying up. When the usual spiropyrans, such as **1**, are dissolved in polar solvents, such as ethanol, acetonitrile, or DMF, some of the spiropyran molecules exist as the colored open form as the result of thermal equilibrium between the colorless closed spiropyran form and the colored open merocyanine form (Fig. 3). The ethanol solutions of DNA–QAIC and spiropyrans were also colored. Therefore, the spiropyran molecules in DNA–QAIC films are not intercalating in the base pairs, but are just a mixture of DNA–QAIC and the spiropyran.

The absorption maximum of the colored form of **1** in DNA–QAIC film was 557 nm. To the contrary, it was 597 nm in a much less polar polystyrene film. Since the colored form of spiropyran is known to take the zwitterionic merocyanine form (phenolate anion and ammonium cation), rather than the isoelectronic neutral form (methylenecyclohexadienone and ani-

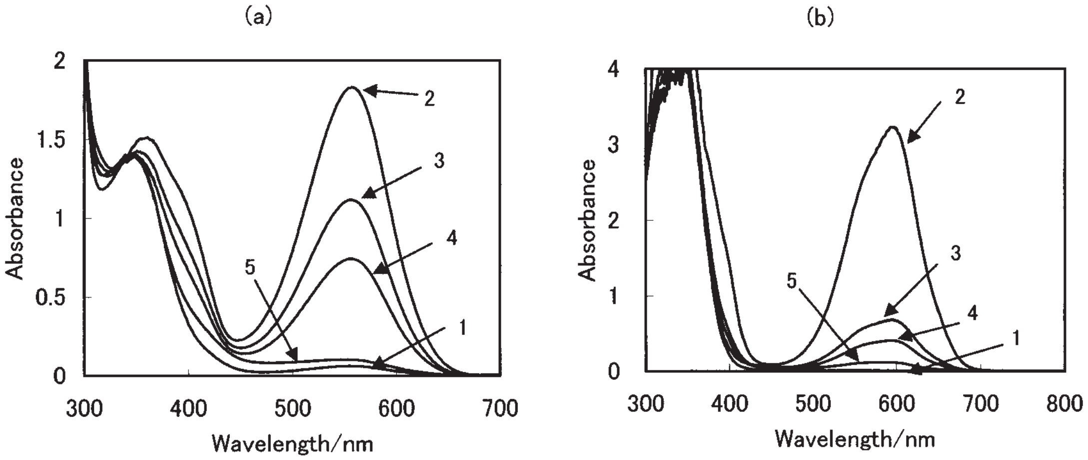


Fig. 2. Absorption spectra of spiropyran **1**. (a) In DNA–QAIC (**1**/base pair = 0.1: 1.6 mg **1**/55.3 mg DNA–QAIC). (b) In polystyrene (9.42×10^{-2} mol dm^{-3}: 1.6 mg **1**/55.3 mg polystyrene). 1; Before UV (366-nm light) irradiation, 2; just after UV irradiation (10 min irradiation), 3; 1 h after irradiation, 4; 2 h after irradiation, 5; 1 d after irradiation.

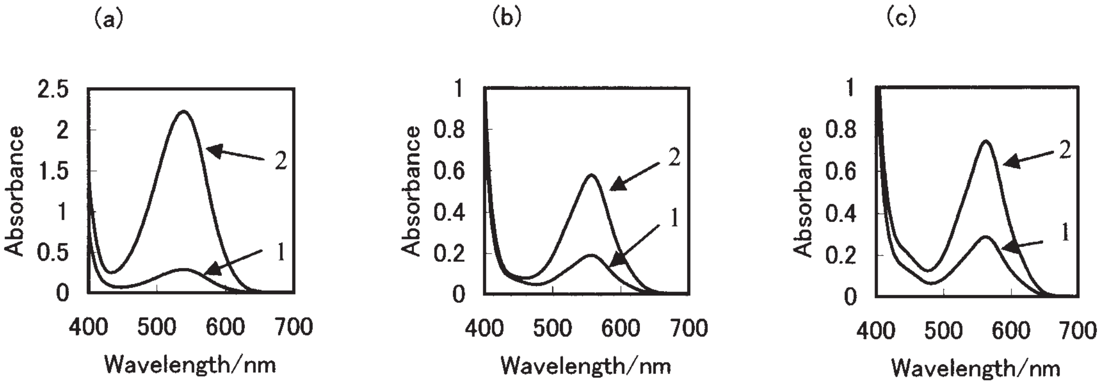


Fig. 3. Absorption spectra of spiropyran **1** in polar solvents. (a) In ethanol. (b) In acetonitrile. (c) In DMF. 1; Before 366-nm light irradiation, 2; After 366-nm light irradiation (10–15 min).

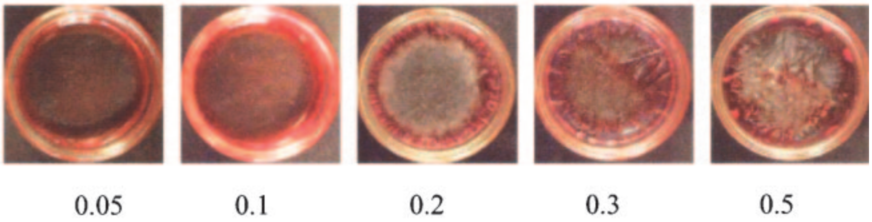
line), its absorption maximum shows a hypsochromic shift when it is placed in a more polar medium. Because the absorption maximum of the colored form of **1** in ethanol, acetonitrile, and DMF are 538 nm, 557 nm, and 563 nm, respectively, the polarity inside the DNA–QAIC film is almost the same as that of acetonitrile ($E_T(30)$/kcal mol^{-1} is 45.6).[21]

When the ratio of the number of molecules of **1** to DNA base pairs was 0.2, the film could no longer be homogeneous. The spiropyran separated out from the mixture to form an opaque film. This is shown in Fig. 4(a). To the contrary, when the spiropyran **2** was used, the film was transparent until the ratio of the **2**-base pair was up to 0.5 (Fig. 4(b)). Apparently the ammonium sulfonate moiety has a large miscibility with the DNA–QAIC film. It is obvious from Fig. 5 that the amount of the spiropyran **2** incorporated in the film as the merocyanine form increased with the increment of the ratio. However, the coloration by UV irradiation was saturated when the ratio increased, probably because of an internal filter effect by the merocyanine form. The fading rate of **2** in DNA–QAIC (Fig. 6), the lifetime of the colored form being calculated to be 1.8 h (again be neglecting the coloration rate constant), was comparable to that of **1** (2.2 h) in DNA–QAIC (Fig. 2(a)).

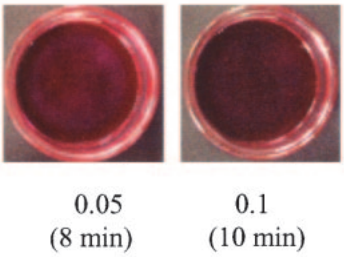
When the UV-irradiation and thermal bleaching cycles were applied to the DNA–QAIC film incorporating **1** several times, the absorbance of the merocyanine form after UV irradiation gradually decreased (Fig. 7). Although a similar decrease in polystyrene film was observed, it was slower than that in DNA–QAIC film. Spiropyran **1** underwent some degrading reactions more easily in complexly functionalized DNA–QAIC film than in simple polystyrene film.

When the spirooxazine **3** was incorporated in DNA–QAIC, the film was colorless and transparent. Although the blue color

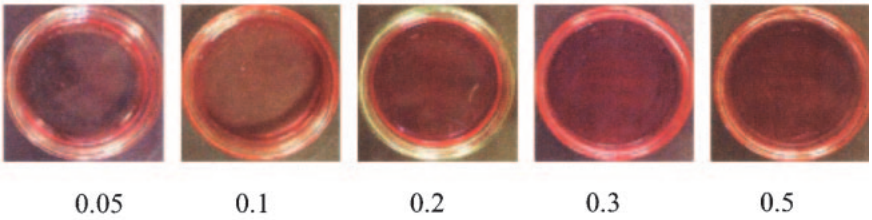
(a) Before 366-nm light irradiation.



After 366-nm light irradiation.



(b) Before 366-nm light irradiation.



After 366-nm light irradiation.

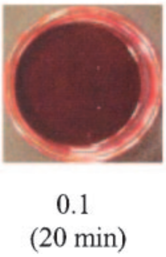


Fig. 4. Spiropyrans in DNA–QAIC films. (a) **1**. (b) **2**. Numbers are the molar ratio of spiropyran to the DNA–QAIC base pairs.

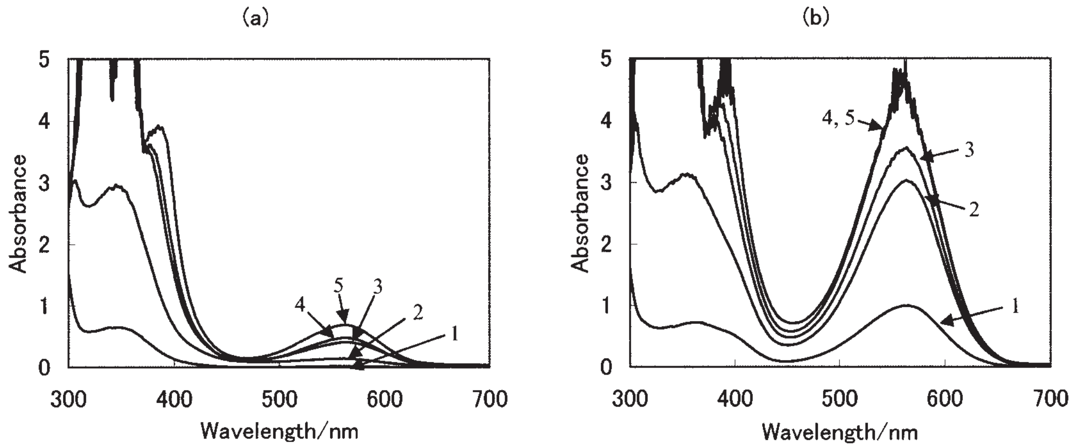


Fig. 5. Absorption spectra of spiropyran **2** in DNA–QAIC. (a) Before irradiation. (b) After 366-nm light irradiation (at maximum conversion. Irradiation time: 1; 8 min, 2–5; 15 min). Molar ratio of **2** to the DNA–QAIC base pairs: 1; 0.05, 2; 0.1, 3; 0.2, 4; 0.3, 5; 0.5.

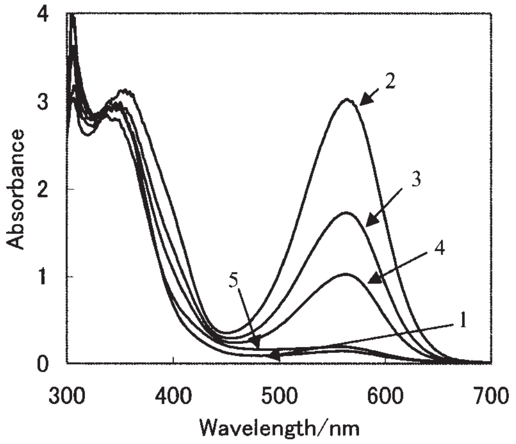


Fig. 6. Absorption spectral change of spiropyran **2** in DNA–QAIC (molar ratio of **2** to the base pairs is 0.1). 1; Before UV (366-nm light) irradiation, 2; just after UV irradiation (15 min irradiation), 3; 1 h after irradiation, 4; 2 h after irradiation, 5; 1 d after irradiation.

of **3** was observed immediately after 366-nm light irradiation, it completely faded within 10 to 15 s at room temperature. The fading rate of the colored form of **3** in DNA–QAIC film was so rapid that the thermal change in the absorbance at 600 nm, where **3** should have absorption, was hardly measurable with the usual spectrometer. On the other hand, the lifetime of **1** of thermal color fading at room temperature in a DNA–QAIC film, calculated from the data of Fig. 2(a), was 2.2 h. It has been reported that the rate constant of decoloration of **1**[22] at 20 °C in ethanol is 2.81×10^{-4} s^{-1}, while that for **3**[23] under the same conditions is $(7 \pm 3) \times 10^{-2}$ s^{-1}. The lifetime of the colored species of **1** is therefore about 1 h, while that for **3** is about 10 to 25 s in ethanol at 20 °C. While the decoloration of **1** was significantly retarded by introducing **1** into DNA–QAIC, the decoloration of **3** was not significantly affected. Different from spiropyrans, the electronic structure of spirooxazine **3** was known to be neutral (methylenecyclohexadienone and aniline) rather than zwitterionic (phenolate and ammonium). Therefore, the very slow thermal color fading of **1** and **2** came from a favorable stabilizing contact interaction on the merocyanine form by the polar DNA–QAIC matrix, which in turn made DNA–QAIC a viscous medium.

However, the stabilizing effect may reduce the free reaction volume during photoirradiation. In order to assess the free vol-

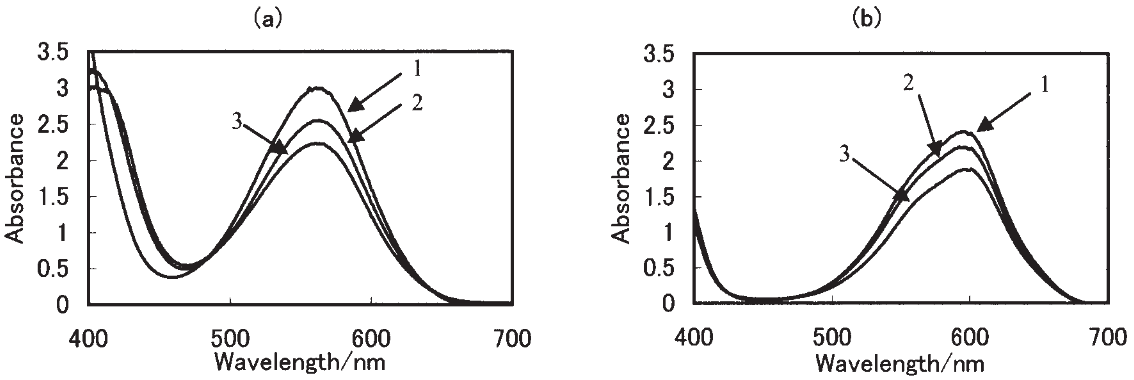


Fig. 7. Change in absorption spectra of spiropyran **1** after repeated 366-nm light irradiation (Handy lamp, 10 min each). (a) In DNA–QAIC (**1**/base pair = 0.1); (b) In polystyrene (6.1×10^{-2} mol dm^{-3}). Numbers; repeated cycles.

ume of photoreaction of spiropyran **2** in DNA–QAIC, a differential scanning calorimetry measurement of DNA–QAIC with **2** above room temperature was carried out. In addition to a broad endothermic peak attributed to the loss of water (94 °C as the peak temperature: when the measurement was repeated on the same sample, it was not observed for the second time), a small endothermic peak (172 °C for DNA–QAIC with **2**) was observed. However, just a few degrees centigrade above it, the film started to decompose. When the film was subjected to an observation with a polarized microscope under the crossed nicoles condition at elevated temperature, no sign of the existence of a liquid crystalline state or an isotropic liquid phase was observed below the decomposition temperature (180 °C). Therefore, the film was obviously rather more amorphous than liquid crystalline in the range of room temperature to 180 °C when it started to decompose. Because it has been stated that DNA–QAIC film is rich in free reaction volume,[2] photochromic reactions of spiropyrans could occur.

Conclusion

Two thermally reversible photochromic spiropyrans, **1** and **2**, were incorporated in organic-solvent-soluble DNA–QAIC powder and films. Although the crystals of spiropyrans did not show any color change upon 366-nm light irradiation, the powder and the films showed thermally reversible photochromism. The spiropyran molecules in the powder took a closed form, and were concluded to be intercalating between the DNA base pairs. On the other hand, spiropyrans incorporated in DNA–QAIC films behaved as in polar organic solvents, because they were not intercalating.

Transparent and self-standing photochromic films containing spiropyran **1** or **2** were prepared. Spiropyran **2** was soluble in DNA–QAIC film much more than **1**.

While the decoloration of spiropyrans **1** and **2** in DNA–QAIC films took several hours, the spirooxazine **3** incorporated in a film faded within seconds.

Experimental

Samples. DNA Na salt (average MW: 34000) obtained from salmon milt was purchased from Nichiro, Co. Ltd. The DNA content in the sample was 82.63 wt %. The phosphate residue in DNA was calculated to be 2.55×10^{-3} mol g^{-1}. Commercially available dodecyltrimethylammonium chloride was used as received as a quaternary ammonium salt to prepare DNA–QAIC powder and films. The following commercially available compounds were used as spiropyran derivatives: 1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] **1**, 3′,3′-dimethyl-6-nitro-1-(3-sulfopropyl)spiro[2*H*-1-benzopyran-2,2′-indoline] triethylamine salt **2**, and 1′,3′,3′-trimethylspiro[indoline-2,2′-[2*H*]naphtho[2,1-*b*][1,4]-oxazine] **3**.

Preparation of DNA–Dodecyltrimethylammonium Ion Complex (DNA–QAIC) Powder Containing Spiropyran Derivatives.[7] The addition of dodecyltrimethylammonium chloride (29.2 mg, 0.11 mmol) to a 5 mL aqueous solution containing DNA (39.5 mg, 0.10 mmol for the phosphate unit) formed precipitates. To this mixture was added a solution of **1** (16.1 mg, 4.99×10^{-2} mmol) in 5 mL of chloroform, and the resultant three-phase mixture was stirred at about 40 °C for 1 d. The resultant precipitate was collected by filtration, and washed with water and then chloroform. A DNA–QAIC powder incorporating **1** (52 mg) was obtained.

A DNA–QAIC powder (17.4 mg) containing spiropyran **2** was also prepared from 29.2 mg of dodecyltrimethylammonium chloride (0.11 mmol), 39.5 mg of DNA (0.10 mmol base pair), and 26.7 mg of **2** (5.02×10^{-2} mmol) in a similar manner.

Preparation of DNA–QAIC Films Containing Spiropyran Derivatives. The addition of dodecyltrimethylammonium chloride (881 mg, 3.34 mmol) to an aqueous solution (150 mL) of DNA (983 mg, 3.04 mmol for the phosphate unit) formed precipitates, which were collected by filtration, washed with acetone, and dried to give 1.58 g of the DNA–QAIC complex (94%). The thus-obtained powder is soluble in methanol and ethanol. The spiropyran **1** (1.6 mg, 4.96×10^{-3} mmol) was added to a solution of DNA–QAIC (55.2 mg, 0.10 mmol base pair: 10 eq with regard to **1**) in 3 mL of a mixed solvent (chloroform/ethanol = 2/1 (v/v)), and the resulting solution was thoroughly stirred at room temperature to make a homogeneous solution. The solution was then cast into a flat glass Petri dish (diameter 2.5 cm), and the solvent was evaporated at ambient environment in the dark to give a DNA–QAIC film incorporating the photochromic compound. The thickness of the film (**1**/DNA base pair is 0.1) was ca. 20 μm.

DNA–QAIC films containing **1** in various concentrations (molar ratio of **1**/DNA base pair = 0.05, 0.2, 0.3, and 0.5), and DNA–QAIC films containing **2** in various concentrations (molar ratio of **2**/DNA base pair = 0.05, 0.1, 0.2, 0.3, and 0.5) were prepared in a similar manner. DNA–QAIC films containing **3** (molar ratio of **3**/DNA base pair = 0.1) were also prepared in a similar manner.

Photoirradiation to the Powder or Film of DNA–QAIC Containing Spiropyran Derivatives. For powders and some of films, irradiation was carried out by a handy-lamp of 366-nm light for TLC detection, for 5 to 10 min. The power of the light was 1.17 mW cm^{-2}. For films and solutions, the emission line of 366 nm of a 500-W high-pressure mercury lamp (Ushio Electric) was separated by filters (Toshiba UV-35, UVD-35, a 1-cm path-length quartz cell containing aqueous $CuSO_4$ (50 g dm^{-3}), and a 5-cm path-length Pyrex water filter). The power of the light was 5.2 mW cm^{-2}. DNA–QAIC and polystyrene films were irradiated with UV light while they were sticking on the Petri dish.

DSC Measurement. PerkinElmer DSC7 was used for differential scanning calorimetry measurements of DNA–QAIC film containing spiropyran **2** (**2**/DNA base pair is 0.1).

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