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Effects of DNA on the Formation of J-Aggregates of Pseudo-Isocyanine

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We prepared the solution and film samples including pseudo-isocyanine (PIC), DNA and polyvinylalcohol (PVA) and conducted the absorption and circular dichrosim spectroscopies. The effects of DNA on the formation of J-aggregates were investigated by the dependence of optical spectra on the concentration of the dye and DNA. From the results, we found that small amount of DNA promotes the formation of J-aggregates in solution, and the maximum J-aggregate peak was obtained with the PIC iodide concentration of 1.31×10^{-3} *mol/l, which is less concentrated than usual conditions. We also succeeded to fabricate PVA films including 1.2% dye and 0.5% DNA by a spin coating method from the solution, demonstrating the J-aggregate peak and a circular dichroism signal.*

Keywords CD spectrum; DNA; J aggregates; PIC; pseudo-isocyanine

Introduction

The possibility of new optical devices using DNA has attracted attentions in recent years, since a formation method for DNA-surfactant complex films was developed [1,2]. Many organic dyes intercalated or bound to the double helix structure have been found to show the enhancement of optical functions of the dyes. One of the most important effects is that the light emission from the dyes incorporated in DNA strands is strongly enhanced. This is because DNA can prevent the aggregation among the dyes, and fluorescence quenching is strongly suppressed by attracting the dyes into DNA strands or grooves by electrostatic interaction as schematically described in Figure 1. This effect can be considered as an example of controlling molecular distribution in a matrix.

The specific structures of DNA can not only be applied to control the alignment of dye molecules, and it is also possible to detect a DNA sequence from the optical properties of dyes incorporated. Until now, Armitage have succeeded to prepare the J-type and/or H-type alignments of several cationic cyanine dyes along the minor grooves of artificial DNA sequences and showed the possibility of controlling molecular ordering by DNA [3].

On the other hand, as well-known in molecular scientists, intermolecular interaction modulates the electronic wavefunctions of molecules and leads to significant changes of optical characteristics. The most extreme case is the formation of

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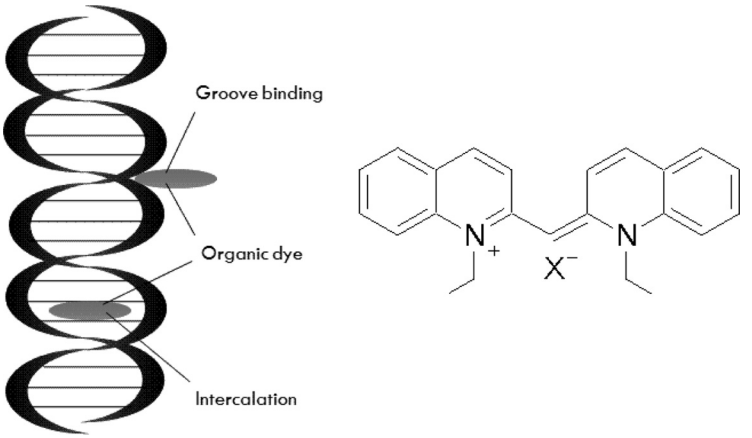

Figure 1. A schematic diagram of intercalation and groove binding of dye molecules into DNA, and molecular structure of 1′1-diethyl-2′2-cyanine halogenide (PIC-X). We used Br and I as X.

J-aggregates of some cyanine dyes which show very narrow optical absorption and emission bands due to the delocalization of molecular excitons in quasi one-dimensional strings. Such co-operated excited states are also known to give large and fast nonlinear optical responses and superradiant emissions [4,5]. The condition of the J-aggregate formation is so sensitive to solvent, dye concentration, temperature, pH and so on that the addition of DNA will influence the formation of J-aggregates both in solutions and solid films [6]. Therefore, it is important to investigate the condition to obtain the strong and narrow J-peaks for future application to optical devices.

In this study, we have chosen pseudo-isocyanine bromide (PIC-Br) and iodide (PIC-I), because the J-band of these dyes is narrow and sharp in comparison to the other cyanine dyes and had been most widely investigated until now. We studied the formation condition of the J-peak under the influences of DNA in solutions and films, mainly by using absorption and circular dichroism (CD) spectra. Molecular structure of the dye is given in Figure 1.

Sample Preparation

We prepared the solution samples for the optical measurements and also as the ingredients for film fabrication. The dyes PIC-I and PIC-Br were purchased from Aldrich and Hayashibara, respectively, and were used without further purification. The purified DNA extracted from salmon spermary was provided from Ogata Research Laboratory (Chitose, Japan). We used 4:1 mixture of water and methanol as a solvent for PIC-I and pure water for PIC-Br, because PIC-I cannot be well dissolved in pure water. We also dissolved polyvinylalcohol (PVA) in the solvent, because PVA suppresses the precipitation of the dye promoted by the addition of DNA.

The preparation procedure is described in the following. First, we dissolved the dye and PVA in the solvent before we added a small quantity of water solution of DNA (3.0×10^{-4} g in 0.1 ml as a unit). Because of the difference of solubility,

the dye concentration depends on the type of the counter cations. We often refer 'case I' for PIC-I, and 'case Br' for PIC-Br. (case I) The concentrations of PVA and the dye were 0.048 and 6.0×10^{-4} g/ml, respectively. The latter value corresponds to 1.31×10^{-3} mol/l and this is almost the saturation concentration. We took 5 ml of it for the measurements. (case Br) The concentrations of PVA and the dye were 0.0406 and 4.1×10^{-4} g/ml, respectively. The latter corresponds to 1.00×10^{-3} mol/l. We took 10 ml.

Film samples were prepared by spin coating on glass substrates. We used the solution including 4 units and 7 units of DNA water for case I and case Br, respectively. Therefore the concentration ratios of the compositions were calculated to be PVA: DNA: PIC-I = 100: 0.5 : 1.2, and PVA: DNA: PIC-Br = 100: 0.5 : 1.0. Spinning speed was 1,500 rpm for both cases. We also fabricated films without DNA for comparisons.

Experimental Results

For the absorption measurements of solutions by UV-Vis spectrometer, we used a separate type quartz cell with 0.1 mm optical pathlength (Starna 20/O/0.1) because the dye concentration was rather high. For the case I, DNA concentrations correspond to $0 \sim 4.2 \times 10^{-4}$ g/ml and the highest concentration is equivalent to 6.3×10^{-4} b.p. mol/l (calculated by using the average molecular weight of one base pair).

The absorption spectra are shown in Figure 2. Three peaks at 460, 490 and 525 nm have been assigned to the absorption peaks of monomer. A sharp peak observed on the longer wavelength region is due to the delocalized excitons in J-aggregates. As known from the figure, the position and linewidth of the peak are 580 nm, and 6 nm, respectively, and these values do not depend on the DNA concentration. The spectral shape of the short wavelength region shows slight distortion at the concentration where strong J-band appears. This effect has been assigned to

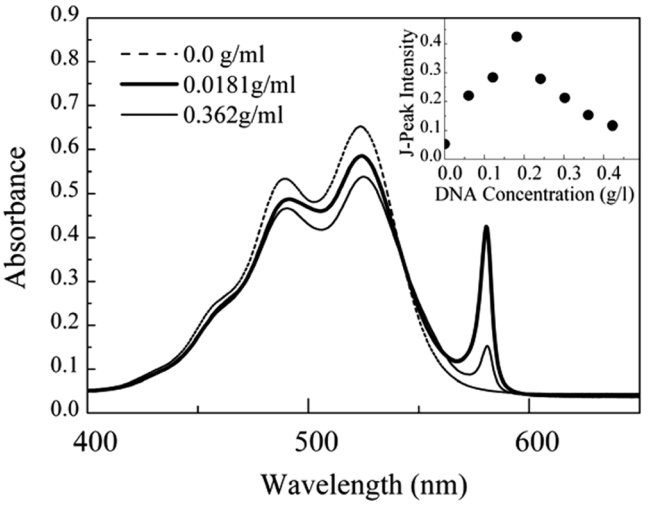

Figure 2. The absorption spectra of PIC-I in mixture of water and methanol with and without DNA. PVA is also dissolved in order to prevent crystallization of the dye molecules. (Inset) Dependence of the peak intensity at 580 nm on the concentration of DNA.

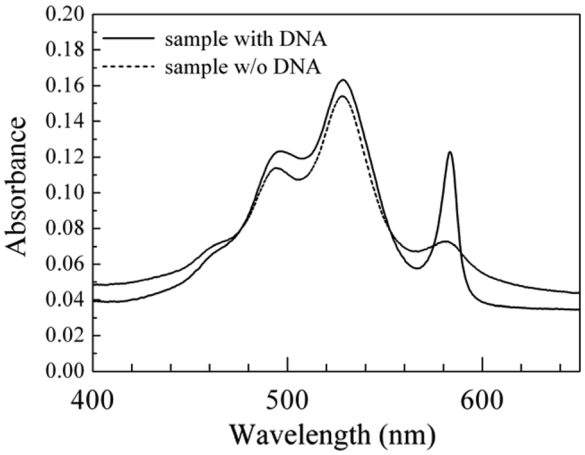

Figure 3. The absorption spectra of the film composed of PVA and PIC-I with and without DNA.

the influence from the higher energy branch of the aggregated molecules. The dependence of J-peak height on the DNA concentration is depicted in the inset of Figure 2. We can conclude that some small amount of DNA enhances the formation of J-aggregates, but too much amount of DNA disaggregates them. This means that there is an optimum DNA concentration for obtaining J-aggregates, and this concentration is quite low, that is, almost comparable to the dye concentration.

When we used methanol as a solvent, we could not find any J-aggregation in spectra. The 4:1 ratio of water and methanol has been determined from the solubility and the conditions for emergence of J-peaks, although the details will not be given in this paper.

Figure 3 depicts the absorption spectra of the films formed from the solution sample. This sample also shows the J-aggregate peak at 583 nm. The linewidth

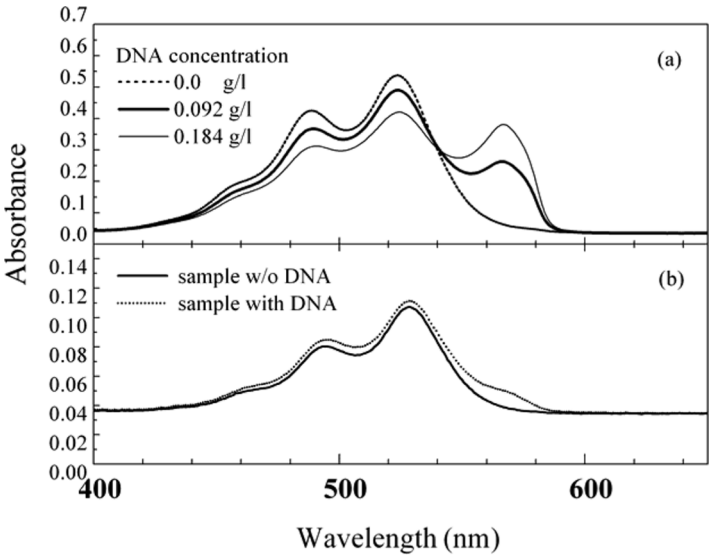

Figure 4. Absorption spectra of the (a) solution and (b) films based on PIC-Br dye. Details of sample composition are given in text.

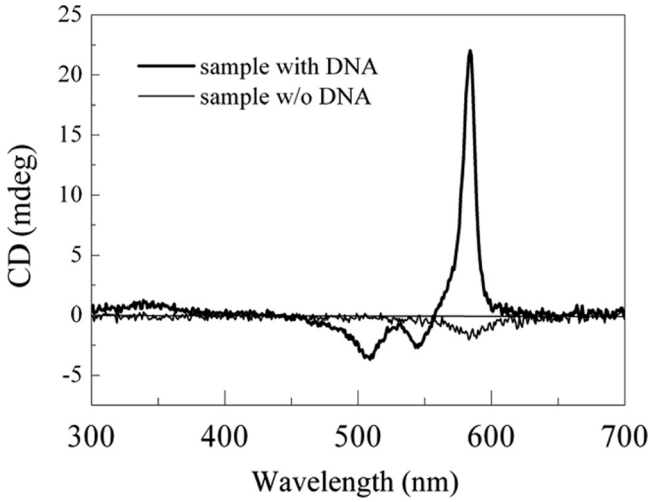

Figure 5. Circular dichroism spectrum for the film samples including PIC-I, PVA and DNA. The spectrum for the sample without DNA is also shown for comparison.

of the peak is 9 nm and that is slightly broader than the width for the solution. The peaks at shorter wavelength side are located at 498 and 528 nm, and these are apparently corresponding to the monomer peaks observed in solutions.

We also made similar measurements for PIC-Br, and the results are shown in Figure 4(a). In this case, we found that J-aggregates were formed but its spectral width was much broader than those for the case I. As given in Figure 4(b), similar situation was observed in a film form, that is, a shoulder at around 580 nm must be a J-peak that could not be observed without DNA. Therefore, we must recognize that slight difference of the types of counter ions gives more serious effects than normally expected.

We also observed the CD spectrum for the film samples. Because of the optical activity of DNA, the dye attached to the strand may give CD signal and it will evidence the interaction between DNA and the dye. Figure 5 shows the CD spectra obtained from the same PIC-I film as used for the absorption measurements by using a CD spectrometer (J-820, JASCO). We can clearly show that there is a CD signal at the wavelength of 584 nm which is corresponding to the J-peak, and a very weak and negative signal was detected for the sample without DNA, which reflects the weak J-peak observed in the absorption spectrum. There are other negative two peaks at 508 and 545 nm, and these values do not correspond to the absorption peaks shown in Figure 2. Therefore, these two peaks can be assigned to the higher energy branch of the Davydov splitting caused by a herringbone structure of the aggregates and these absorption peaks have been hidden in the bands of residual monomers [4].

Discussions

The dependence of the absorption spectra of PIC dyes on DNA concentration shows that there is the optimum amount of DNA which enhances the formation of J-aggregates. Excess DNA may suppress the J-aggregate formation because most of dye molecules are disaggregated and attracted to DNA strand by electrostatic force.

We have already observed similar effects by using other cyanine dyes in solution including DNA [7]. In our former study, we have added DNA into water solutions of diethylthiacarbocyanine and its relatives, and observed the aggregate formation and their disaggregation from optical absorption and photoluminescence spectroscopies. For the current case, the situation is slightly different, that is, we incorporated PVA as well as DNA. However, it also suggests the importance of the role of DNA for molecular alignments.

The behavior of short wavelength peaks of Figure 2 and Figure 4(a) seems a little contradictory, because the monomer peaks should grow by the addition of excess DNA if it stimulates the disaggregation of molecules. For the case of the films in Figure 4(b), both J-peak and monomer absorptions are increased with DNA increase. One possible reason is that the oscillator strength of the dye varies by the interaction with DNA strands, but more meticulous measurements will be required to eliminate possible artifacts such as the pathlength fluctuations of separate type quartz cells.

As shown in Figure 5, the strong CD signal at the J-peak wavelength can be an evidence of the interaction between dye molecules and DNA. But there is a small CD peak with the opposite sign was observed in the film without DNA, suggesting the different chiral conformation of the aggregates. Indeed, PIC and related materials sometimes spontaneously forms helical structure even in conventional environments and expresses CD signals, for example, in PVA films or in solutions, therefore we might hesitate to imply that the CD signals are completely the results from the dye-DNA interaction [8,9]. Further studies will be required to clarify the interaction effects.

Until now, there have been many studies on the J-aggregates of PIC dyes. Most of recent studies have been conducted on PIC-I because of its easy availability [10–12]. However, it was difficult to make J-aggregates due to its low solubility in water, so additional solvents or sodium chloride as a buffer were incorporated to obtain the J-peaks. On the other hand, a few studies had been done for the J-aggregates in films except the LB films made by several photosensitive dyes [9,13,14]. One exception was the work conducted by Kobayashi's group who succeeded to fabricate PVA films doped with PIC-Br which shows the strong J-aggregate peak [15]. In our case, we observed a sharp J-peak for the complex films made from PVA, PIC-I and DNA and its width was much narrower than those for the PIC-Br samples. The concentrations of PIC-dyes in our samples were much smaller than other cases; the fact means that we could prepare the material having J-characteristics with a low concentration of the dye by incorporating DNA as a component. The emergence of J-aggregates in low concentration might be important and to establish the recipe for obtaining and controlling the J-peaks in film forms will be useful for the future developments of new applications.

Conclusion

In this work, we have prepared the solutions and films including PIC dyes, PVA and DNA, and have changed systematically the composition of the materials, that is, mainly the DNA concentration. From the measurements of absorption spectra and the supplemental CD spectrum study, we succeeded to find the optimized conditions for forming of the J-aggregates of PIC dyes in solution and film samples. We confirmed that the addition of DNA both in solutions and films plays an important role to promote the J-aggregate formation, and that it is possible to

obtain the materials demonstrating J-peaks with lower concentration of the dye by incorporating DNA in the solution and films. These results would be important for the development of novel optical devices such as optical switches, specific light sources and so on.

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