Photo-induced birefringence and photo-induced transparency observed in azo chromophores embedded in DNA complex composites

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DNA complex is a promising for compact wavelength tunable laser sources. In order to facilitate practical wavelength tuning, azo materials were incorporated into the complex via monomer doping and blending with an azo copolymer. An azo moiety showed photo-induced birefringence and transparency when it was doped in the mixture of DNA complex and PMMA, or incorporated as a side-chain of a copolymer blended with the complex, while such effects were hardly observed when the dye was simply mixed into the DNA complex. The composite films gave birefringence as high as 0.0025 and 30% reduction of absorbance under the excitation of 30mW/cm^2. Two types of DNA-based materials including azo moiety were stained with rhodamine dyes, showing light amplification under optical pumping with 2 or 10mJ/cm^2 fluences.
Key words: DNA complex, thin film dye laser, azo dyes, photoisomerization, birefringence

1. INTRODUCTION

DNA complexes composed of DNA and cationic surfactants are promising materials for medium of solid-state thin film dye lasers, because of high light amplification efficiency and superior durability caused by interaction of incorporated dyes with DNA strands [1]. Wavelength tuning mechanism for the laser films was implemented with a dynamic grating formed in azo material locating in an adjacent layer [2].

It would be beneficial for practical use if single-layered laser devices are fabricated by co-doping light emitting dye and azo dye in the same layer. It seems possible simply by making films doped with two kinds of dyes. However, it is necessary to confirm the photo-response of azo materials in DNA complexes and to make adequate selection for each dye to prevent the reabsorption of emitted photons. There have been several preceding studies regarding photo-induced behaviors of an azo molecule disperse red 1 (DR1) in DNA complex, showing relatively weak responses even under strong laser irradiation [3,4]. Further, there was no reports published regarding to the fluorescence reduction of dyes co-doped with azo materials.

In order to confirm light amplification of dyes surrounded by azo molecules in single layered devices, and to overcome the weak response of the azo dyes in the DNA complex, we present in this proceeding an attempt to solve the problems through modifying the composition of DNA based matrix surrounding the azo moiety [5,6]. We fabricated five types of samples composed of DR1 and host polymers, and studied their photo-induced birefringence (PIB) and photo-induced transparency (PIT).

Strong signals were observed when DR1-PMMA copolymer was mixed with the DNA complex, contrary to the weak and fast response of monomeric DR1 in the DNA complex. With rhodamine dyes doped in the film with an immersion method, amplified spontaneous emission (ASE) was demonstrated, showing high promise of the material to thin film dye lasers.

Table 1. Five types of composite films prepared.

#	sample	Dye conc. (wt%)	Thickness (μm)	OD at 532 nm	κ_0 at 532 nm	Peak wl. (nm)
1	DR1/DNA-CTMA	2	1.1	0.217	0.0192	507
2	DR1/PMMA	2	1.3	0.198	0.0149	494
3	DR1/DNA-CTMA+PMMA	2	0.93	0.311	0.0326	504
4	pDR1/DNA-CTMA	3	1.06	0.245	0.0225	488
5	pDR1/PMMA	2	1.2	0.152	0.0123	473

2. SAMPLE PREPARATION AND EXPERIMENTAL METHODS

Table I shows the summary of basic characteristics of sample films. DR1 was simply doped in two types

of polymers in the samples 1 and 2. For the sample 3, DR1 was doped in a blend of PMMA(20%) and DNA-CTMA(80%). In other two cases, a copolymer, poly[(methyl methacrylate)-co-(Disperse Red 1 methacrylate)] (pDR1) was employed in which 15mol% of PMMA side chain was substituted with DR1. DR1 concentrations were reduced to 2~3wt% by mixing with the other inactive polymers in these cases.

DR1 was purchased from Sigma-Aldrich to be used as it was. DNA was complexed with a cationic surfactant cetyltrimethylammonium chloride (CTMA) with a method described in our preceding papers to obtain the complex DNA-CTMA [7,8]. The PMMA and copolymer pDR1 were also products of Sigma-Aldrich. Molecular weight of PMMA was claimed to be 120,000. The films were prepared with a spin coating method of which details were addressed in other proceedings [5,6].

Figure 1 shows absorption spectra for the five films, where their intensities are normalized by the maximum value of each spectrum. Monomeric DR1 had a peak at 507 and 494nm in DNA-CTMA and PMMA, respectively. The peak wavelength for the sample 3 corresponded to the weighted average value calculated by those of the samples 1 and 2. The fact indicated that DR1 molecules were equally dispersed in two polymers. The peak for pDR1 in PMMA (sample 5) located in shorter wavelength side than the monomeric counterpart (the film 2). The mixture of pDR1 and DNA-CTMA showed the broadest spectrum among all. The extension to short wavelength side was close to that of monomeric DR1 in PMMA, but its tail to long wavelength side was almost the same to DR1 in DNA-CTMA. The fact suggested that the energy level of the chromophore was influenced from both of PMMA backbone and surrounding DNA complex.

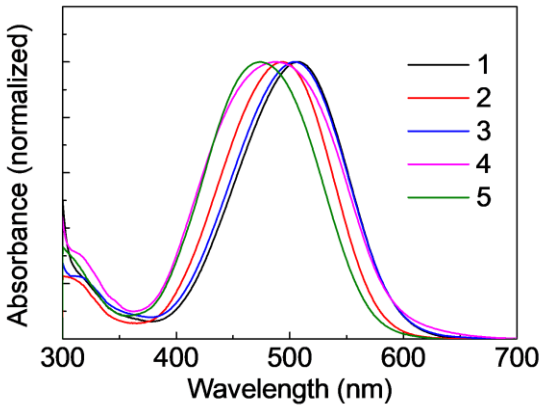

Fig. 1 Normalized absorption spectra for DR1 chromophore in various circumstances.

The measurements for PIB and PIT were made for all the samples. Two green (532 nm) probe beams with horizontal and vertical polarization, and a linearly polarized IR beam (from 783 nm LD) with 45° polar direction from the horizon were injected on a sample position where a pump beam covered the area. Wavelength of the pump beam was 532 nm and its typical intensity was ~30 mW/cm^2. The experimental setup and formulae for the estimation of birefringence and the change of extinction coefficient were described in our former works [5,6,9].

Laser dyes were doped in some of these films with an immersion method [10,11]. The procedure for ASE measurement was described in our former publications [12,13]. The sample 1 and its analogue made with disperse orange 3 (DO3) were immersed into a solution of rhodamine 6G (Rh6G), one of the most important laser dyes. The sample 4 was stained with rhodamine 640 perchlorate (Rh640) with the same way. These films were excited with a pulsed green laser (frequency doubled Nd:YAG). The details of experimental method was given in our recent works [5,6].

3. RESULTS AND DISCUSSION

3.1 Photo-induced birefringence

The results on DR1/PMMA (corresponding to the sample 2) was already published in another paper where a He-Ne source was employed as a probe giving almost the same results obtained with the current system [9]. Monomeric DR1 in DNA-CTMA showed no or very weak birefringence and reduction of absorption as discussed in ref. 5 and 6. In preceding studies by a Polish group, diffraction signals in four wave mixing originating from photo-isomerization of DR1 in DNA-CTMA were observed, where excitation intensities were much higher than our cases [14,15]. These facts indicated that the modulation of refractive index of the typical azobenzene derivative was much weaker when it was embedded in DNA complex.

The results for the other three samples are depicted in Fig. 2. The major constituent of the samples 3 and 4 was DNA-CTMA, and it was blended with PMMA or pDR1. The corresponding value for the sample 2 was 0.0015 which was slightly larger than that for the sample 3. Considering that PMMA occupied only 20% of the whole volume, and that DR1 in DNA-CTMA was inactive, the magnitude was quite larger than that predicted by a simple estimation in which only DR1 in PMMA contributed. The result was also contradictory to those for induced transparency shown below where its magnitude was roughly proportional to DR1 concentration.

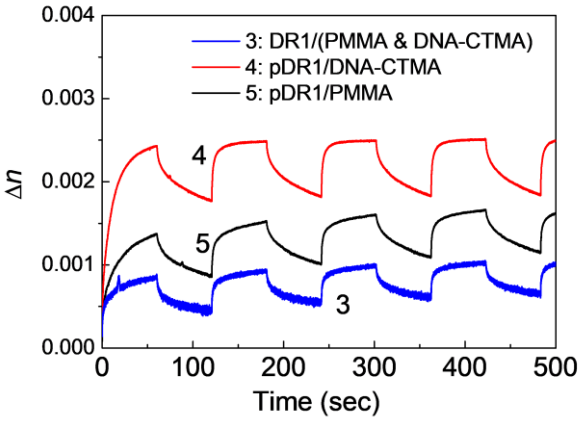

Fig. 2 Photo-induced birefringence observed in three types of films composed of PMMA, DNA-CTMA, and pDR1. Excitation beam was irradiated 1 min after every 1 min break.

The sample 4 gave the highest value among all due to higher density of the moiety. It could be comparable to 5 if normalized by dye concentration. But the sample showed quicker approach to photo-stable state as known from the plateau-like feature during excitation. Influence from DNA-CTMA might contribute to the property. On the other hand, the signal for the sample 3 resembled to that for 5, although the magnitude was smaller.

Material composition was common to the samples 3, and 4, but covalent biding structures of 4 and 5 were the same. If the dynamic behaviors of DR1 was affected by surrounding materials, it follows that DR1 in the sample 3 did not interact with the DNA complex. On the other hand, DR1 moiety attached on the PMMA side chain of the sample 4 should have strong interaction with the complex. It seems not very easy to understand such a situation. Other investigation would be required to clarify the mechanism causing the differences.

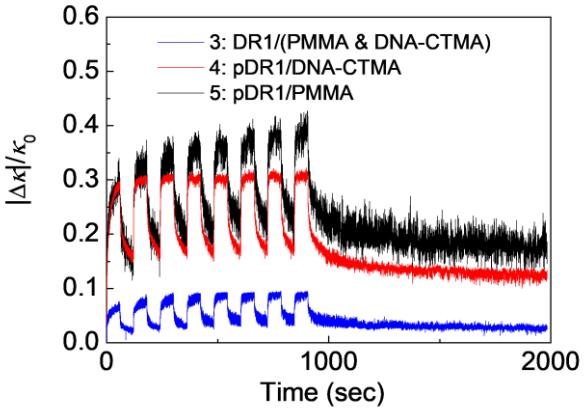

Fig. 3 Reduction of extinction coefficient under the irradiation of excitation light (photo-induced transparency). The signals were monitored simultaneously with those shown in Fig. 2.

3.2 Photo-induced transparency

Photo-induced transparency was studied by monitoring the probe beam intensities under the pump light. The polarization for the two probe beams were set to be parallel and perpendicular to the pump beam. Fig. 3 indicates the results for the three samples common to those for Fig. 2. The result for the sample 2 was omitted, but its shape and magnitude was similar to that for 5. The signal intensity for 1 was negligibly

small.

The maximum reduction of absorbance was about 30~40 % for 2, 4, and 5, while the sample 3 gave smaller change. If only the dye dispersed in PMMA responded to the actinic light, the result meant that only the moieties in PMMA responded, since weight ratio of PMMA was 20%. But such conjecture was contradictory to the results of PIB where Δn value was much larger than that predicted by the same assumption. In spite of several questions, we can conclude that the same mechanism was dominant for both effects, that is, PIB and PIT, because signal shapes in two experiments were quite similar for these samples.

In our former study on DR1/PMMA, it was found that the *trans-cis* transition dominantly contributed to the optical constant modulation, and molecular orientation was much slower process of which effects accumulated slowly during the order of several ten seconds or minute [9]. In this study, the same discussion could be applicable.

3.3. Amplified spontaneous emission

We succeeded in ASE observation from Rh6G in DO3/DNA-CTMA and Rh640 in pDR1/DNA-CTMA. Output peak intensities are plotted in Fig. 4 against input where a leap of the value indicated the threshold of each sample. When no azo materials were incorporated, the threshold value for Rh6G/DNA-CTMA was about 1mJ/cm^2 which corresponded to our old work [16]. Co-doping of DO3 increased the threshold value a twice, while no ASE was obtained when DR1 was employed which had longer wavelength absorption band. For the case of pDR1/PMMA, Rh640 was incorporated since it had longer wavelength absorption than Rh6G. ASE was observed in this case, even though its threshold was one order higher than the other case.

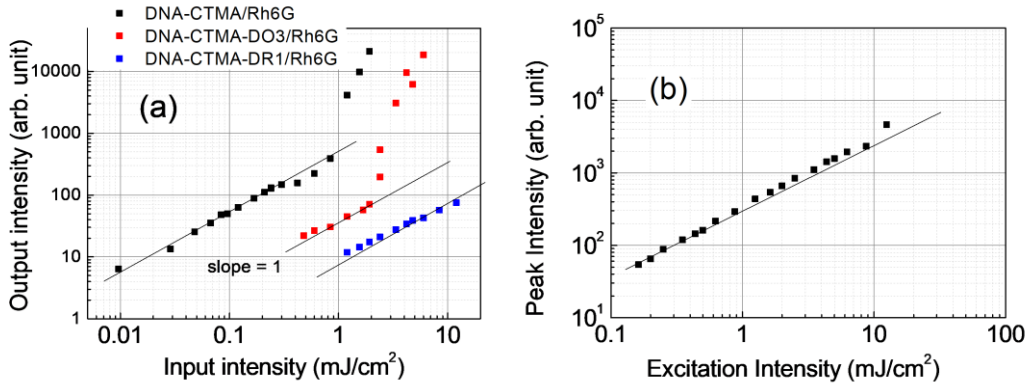

Fig. 4 (a) Output intensity dependence on input excitation for Rh6G doped in DNA-CTMA with or without azo dyes. Lines show linear relationship and leaps occurr at threshold intensity. (b) The result for Ph640 in pDR1/DNA-CTMA where the small leap at the last point indicates the existence of threshold. Narrowing of the emission spectrum was displayed in ref. 5.

Unlike the bi-layered devices we have developed before, laser dye and azo dye located in close proximity in this case. The ASE observation from single layer device certifies that there is no intrinsic problem in realization for single layer tunable compact dye lasers based on the DNA complexes. It might be difficult to use DR1 doped DNA-CTMA because of its poor sensitivity, but the blending of pDR1 with the complex would be a promising method. It is necessary to choose compatible laser dyes to the material, or to develop other co-polymers including azo substituent with wider absorption gap in order to optimize the performance of the lasers.

4. CONCLUSION

In order to develop thin film tunable lasers with DNA complex, photo-response of DR1 incorporated in DNA complex through doping or blending was measured with PIB and PIT. Although the azo dye in DNA complex did not show significant PIB and PIT, strong signals were obtained when it was doped in the mixture of DNA complex and PMMA, or side-chained DR1-PMMA copolymer was blended with DNA complex. Light amplification was demonstrated with films stained with rhodamine dyes through an immersion process. It will pave a way to the realization of compact tunable light sources with relatively fast wavelength scanning mechanism.

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