DNA-based dye lasers: Progress in this half a decade

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ABSTRACT

After the invention of DNA-surfactant films and the proposal of dye doping into them by Ogata, many applications were demonstrated. Among them tunable thin film laser is one of the most attractive functional devices. Development and progress in DNA based lasers after the first observation of amplified spontaneous emission (ASE) by us has been reviewed in a former paper published in 2011.[1] In this proceeding, progresses in the subsequent half a decade are described.

Keywords: dye laser, DNA complex, amplified spontaneous emission, thin film

1. INTRODUCTION

Exotic structure of DNA is considered to be a good template for the incorporation of functional dyes through specific interaction modes between them. Among a lot of possible applications proposed by Ogata, dye lasers are very promising because it would make it possible to realize a small-sized tunable laser sources which will be useful in vast areas of practical uses including industrial, medical and environmental studies. The first demonstration of amplified spontaneous emission (ASE) which meant a laser action without cavity was made by us in 2000.[2] While the dye employed at that time was Rhodamine 6G (Rh6G) which was very popular as laser medium, the optical amplification was also observed in another type of dye, a hemicyanine of which result triggered the investigation on various classes of dyes including rhodamines, sulforhodamine, cyanines, and spiropyrans.[3] Since these results were summarized in our previous review published in 2011, the progresses after the year will be presented in this proceeding.[1]

2. MATERIALS INCORPORATED IN DNA-COMPLEXES

Considering that uncountable organic dyes could be incorporated in DNA or DNA-complexes by various simple routes, numbers of compounds under studies until now were still quite limited. Several newly examined dyes, however, took advantages of their characteristics, showing promising features. In this section, newly developed materials are briefly described followed by a summary in Table 1.

Nonlinear microcrystallites: Organic nonlinear optical (NLO) materials which were widely studied in the past were found to sometimes show luminescence in solutions, in polymer matrices and even in crystalline states. A pyrazole called DCNP known as a NLO crystal was mixed into DNA-cetyltrimethylammonium (CTMA) in several configurations as molecular dispersion and microcrystallites, showing ASE and also lasing with a feedback grating formed in adjacent azo-polymer layer.[4,5] Microcrystallite dispersion in the matrix was found to be effective for random lasing which would be a promising alternative for light source devices.[6]

Biomedical fluorophores: There are a lot of types of dyes used to stain cell or cell organelle, and many of them show fluorescence enhancement when binding to specific parts in the cells. These dyes are utilized widely for analysis or diagnosis of living organization. A large number of cyanines and hemicyanine have been developed for such purposes. Recentely, Pradeep *et al.* employed PicoGreen as a dopant in DNA-CTMA, finding ASE under pumping above 2 or $3mJ/cm^2$.[7] Since so many dyes with special binding characteristics to biomaterials are available for molecular labelling, these are candidates for dye laser application. Characteristics of stimulated emission will provide a novel technique for biological imaging.

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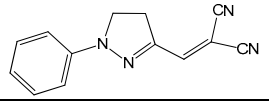
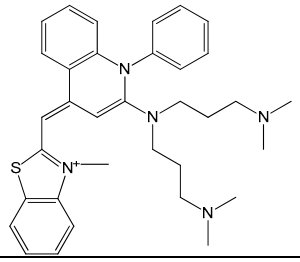
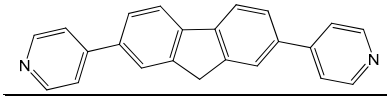
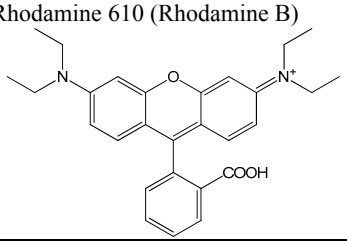
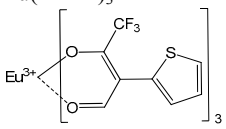
Nanobiosystems: Processing, Characterization, and Applications IX, edited by Norihisa Kobayashi, Fahima Ouchen, Ileana Rau, Proc. of SPIE Vol. 9928, 992806 · © 2016 SPIE · CCC code: 0277-786X/16/$18
doi: 10.1117/12.2237439

Blue or UV light emitter: Most of dyes used in DNA laser have emission color from green to red regions. Therefore, blue light laser will be important to widen the tuning ranges of biomaterial lasers. One example of UV light ASE was reported by Zhao et al.[8] A fluorene derivative was doped into DNA-CTMA to observe ASE peaking at 380nm. To our knowledge, that was the shortest wavelength made with these classes of materials.

Laser dyes: Even well-known laser dyes sometimes show new features in exotic environments. The study on Rhodamine 610 (always denoted as Rhodamine B) mixed up with DNA-CTMA in solution was such an example. Bazaru Rujoiu *el al.* observed lasing from concentrated the solution contained in a thin quartz cell with a feedback by two parallel cuvette walls.[9] They confirmed an improvement of laser coherence with Michelson interferometry, which fact might indicate that there are some roles of organic materials in the basic researches of quantum electronics.

Rare earth chelates: In 2009, Ogata *et al.* reported that fluorescence from some organic europium complexes were enhanced in DNA-CTMA and that the luminescence from trivalent rare earth ions Eu^{3+}, Tb^{3+} and Nd^{3+} were also intensified when they were mixed with DNA in aqueous solutions.[10] Recently, Tsang *et al.* fabricated a $Eu(TTFA)^3$ doped DNA-CTMA fiber waveguide in a quartz tube, observing amplification of 612nm light originating from *f-f* transition in Eu^{3+} under cw pumping at 351nm.[11]

Table 1. List of compounds incorporated in DNA-complex laser devices

Molecular structure	Device configuration	Results	References
DCNP 	a. DNA-CTMA-dye (0.5wt%) b. DNA-CTMA-dye (1.0wt%)	a. laser at 630nm (I_{th} = 11mJ/cm^2) b. random laser at ~ 615nm (I_{th} = 3mJ/cm^2)	[4-6]
PicoGreen 	DNA-CTMA-dye	ASE at 560nm (I_{th} = 2~3mJ/cm^2)	[7]
BPF 	DNA-CTMA-dye (0.25~1.0wt%)	ASE at 380nm (I_{th} = 3mJ/cm^2)	[8]
Rhodamine 610 (Rhodamine B) 	DNA-CTMA-dye (5~15wt%) in butanol solutions	lasing at 575~595nm (I_{th} = 14mJ/cm^2)	[9]
$Eu(TTFA)_3$ 	DNA-CTMA-chelate (2~6wt%)	amplification at 612nm	[11]

3. MATRICES AND FABRICATION METHOD

When DNA-surfactant complexes were prepared, CTMA was usually employed as a counter cation to couple to poly-anionic DNA. Therefore, DNA-CTMA was recognized as a standard complex material in this field. For film fabrication, alcoholic solutions including DNA-CTMA and dyes were usually spun or cast to obtain high quality films. Despite of the usefulness of the protocol, it is worth pursuing alternative surfactants and alternative preparation methods to improve laser performance.

Alternative surfactants: When DNA surfactant complex was synthesized by Tanaka *et al.*, chosen surfactant had flexible structure with multiple ether bonds (1 in Fig.1) to promote molecular alignment by mechanical stretching.[12] When Wang *et al.* reported the structure of dye-doped complexes, in addition to CTMA two other types of surfactants (CP, BDMA) were employed.[13] Effects on ASE or lasing characteristics were studied by Hung *et al*. who used an aromatic surfactant to show the change of ASE peak and also the reduction of threshold value when Rh6G was used as an active molecule.[14] The short-chained surfactant BTMA reduced the threshold value to 0.35mJ/cm^2 which was one order smaller than that for CTMA. On the other hand, as Sznitko *et al.* studied the effects from surfactants (BA and DDCA), ASE shift was not very significant, while the threshold values somewhat scattered.[15] We also examined the materials with aromatic ring or multiple alkyl chains (DMDA, MTOA, and BDMA) to find that ASE peak wavelength and peak width strongly depended on the surfactant type. In that study, water soluble anionic xanthene dye Eosin Y was incorporated as laser medium.[16] Molecular structures of the surfactants and Eosin Y are depicted in Fig.1.

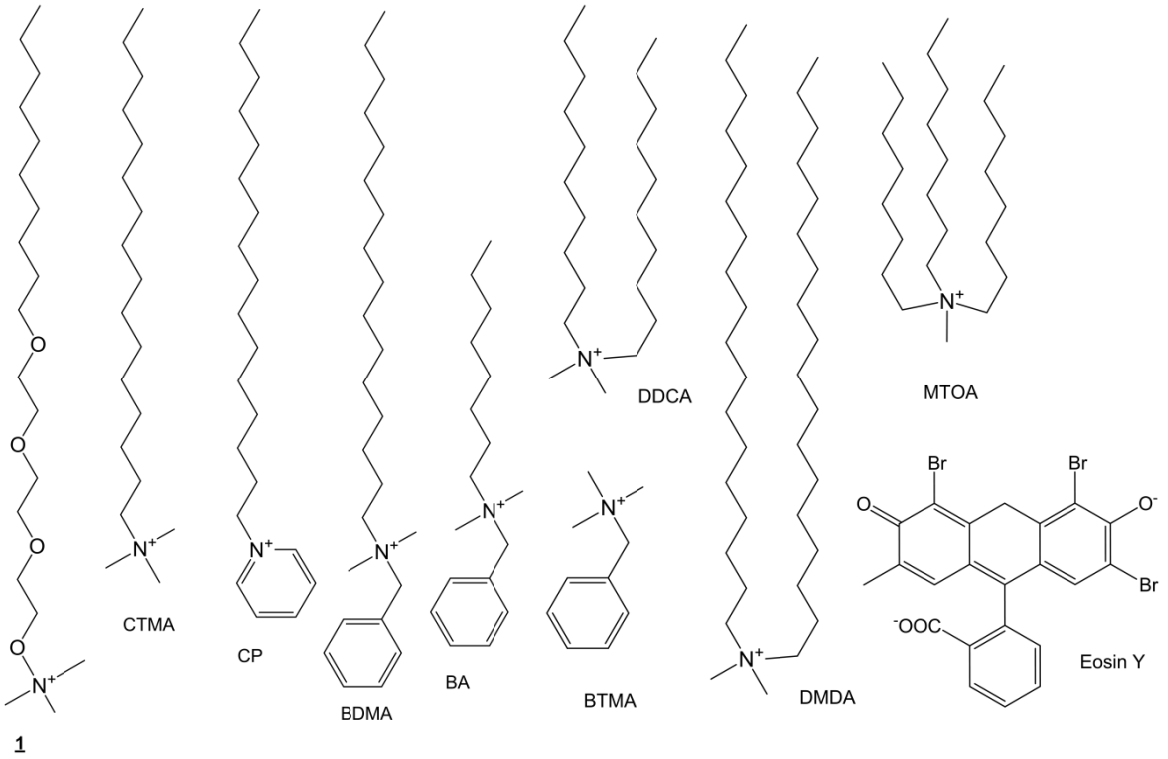


Figure 1. Molecular structures of surfactants used for DNA complex formation, and that of anionic dye Eosin Y.

Pure DNA: Although pure DNA is soluble only to water, it could be a host for dyes when they are also water soluble. Rau *et al* succeeded in the film formation of pure DNA via slow evaporation method. The films with 1% Rh6G showed ASE under optical pumping, although the lifetime was not so long.[17]

Immersion method*:* Most of complex samples were prepared with a standard technique where pre-synthesized DNA-CTMA and incorporating dyes were dissolved in solvents as alcohols to form films by casting methods. We have invert-

ed the process order where the dye and DNA were mixed at first, then followed by complexation process. When the method was applied to a water soluble cyanine dye, device durability was improved.[18] Recently, we developed the third method where DNA-CTMA was immersed in dye solution to allow the dye molecules migrate into the complex films. According to the memory of the author, that possibility was originally pointed by Ogata along with an example at an informal meeting many days ago. Also such possibility was implicitly suggested by the work of Yu *et. al*.[19] The idea was realized by employing Rh6G in water and a hemicyanine in acetone, showing low threshold and long durability.[16,20] Our latest results will be presented in the other talk and the proceeding article in this conference.[21]

4. OTHER TOPICS

FRET excitation: Forster resonance energy transfer (FRET) is a way to excite a molecule in which process the energy absorbed in a donor molecule is sent to an acceptor via dipole-dipole interaction. Because the donor works as antenna for electromagnetic radiation, effective energy capture could reduce emitter concentration required for laser action, thus reduced reabsorption will decrease its threshold value. Ibisate *et al.* first demonstrated ASE from Hemi1 mediated with FRET through Coumarine 480. The estimated threshold 40μJ/cm^2 was quite small compared to other related works.[22] The same group employed the method to a cyanine dye Cy5 to obtain random lasing by combining the complex to micrometer-sized polystyrene beads, decreasing the threshold value to about 10μJ/cm^2.[23] Molecular structures of the Coumarine and Cy5 are shown in Fig.2 along with others referred in this section.

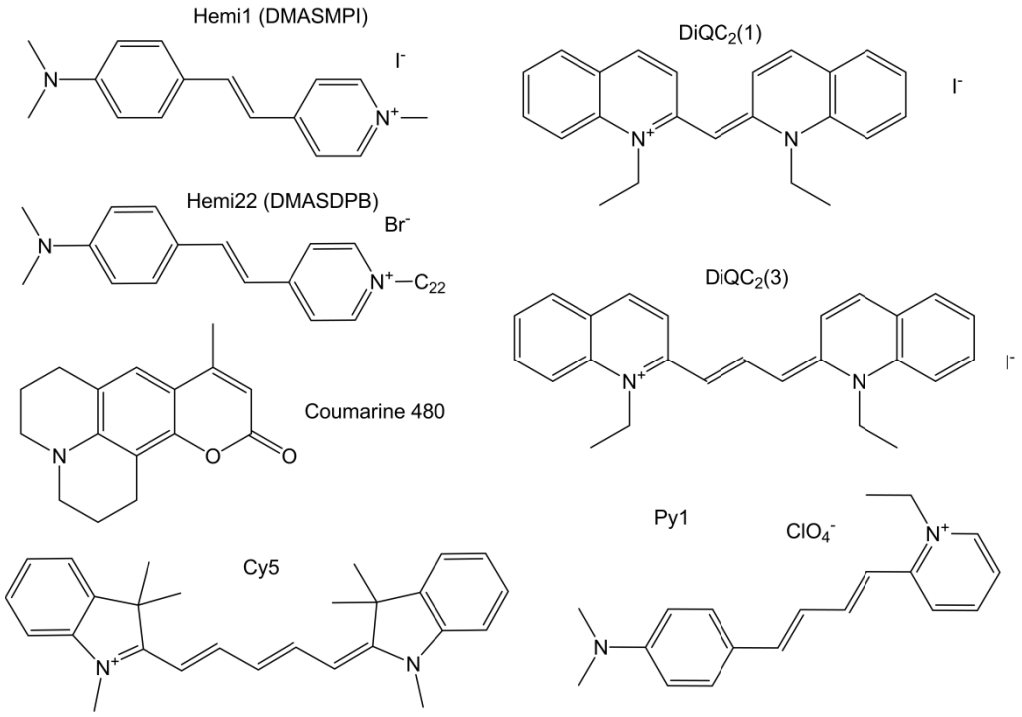


Figure 2. Molecular structures of organic compounds referred in sec. 4.

Random lasers: Random laser is another trend of novel lasers because of low threshold predicted from inherent high Q values. As well as the case described above utilizing microbeads, Consoli *et al.* observed multiple narrow peaks from the DCM doped DNA-CTMA formed on quartz substrates equipped with stripes made by nano-sized TiO_2. Excitation fluence was about 2mJ/cm^2.[24] Microcrystallites are another example where incidentally formed loops in random scattering paths play a role of cavity to give integration of narrow emission peaks, as demonstrated by Mysliwiec *et al.* with DCNP under supports from theoretical investigation. They reported the threshold value about 3mJ/cm^2.[5,6,25] Random

lasing was also induced by surface roughness as given with Rh6G doped in DNA-CTMA or pure DNA in which the threshold values were 30mJ/cm^2 and 5mJ/cm^2, respectively.[26,27]

Dynamic grating: Although wavelength tunability is the most important advantage of dye lasers, implementation into miniature sized systems requires a lot of efforts. In most of studies for DNA-based systems, wavelength tuning has been realized by dynamic gratings formed by interfering beams. In our case, tuning was made in the range of 600-630nm with Hemi22, while tuning in 570-610nm and 670-710nm were performed with two types of cyanine dyes ($DiQC_2(1)$, $DiQC_2(3)$).[28-30] In these cases, grating might be formed by the modulation of gain, giving threshold values around 5mJ/cm^2. Second layer of azo-containing polymer was implemented on Py1/DNA-CTMA layer for the tuning, to show laser emission in red region. However, threshold value was as high as 10mJ/cm^2, because grating must have been kept far away from the active region in order to prevent strong loss of azo dyes.[31] Optimized combination of two dyes is desired to fabricate single layer devices.

Aggregation: Some recent researches reported the influences of dye aggregation on ASE in DNA systems. Since some molecular glasses or crystals show strong photoluminescence as observed in organic LED devices, molecular aggregation will more or less contribute to light emission. Lasing from crystalline DCNP was considered to be an example for such aggregation enhanced luminescence.[6] The idea was extended to molecular cases, when Rh6G in DNA complexes gave random lasing and wavelength change was attributed to aggregation due to molecular concentration.[32] The control of molecular states will give another possibility for DNA-based lasers.

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