Title of Research Project: **Developments of Innovative DNA Photonic Devices**

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Summary

Research 1 Chelation of DNA with novel metals or rare earth metal compounds.

Large amplifications of fluorescence light were attained in the presence of novel metal or rare earth metal cations, especially Eu^{+++} or Tb^{+++} showed a very large fluorescence emission with increasing amount of DNA. These results strongly suggest that electron shells would be twisted and electron state including electron spin would be changed by interactions with nucleic acid bases of DNA. Novel electronic applications of DNA will be open by these results and further research on DNA electronics is required.

Research 2 Novel crosslinkers of DNA devices to improve mechanical strength

UV curable lipids containing acrylate groups is being synthesized to prepare UV curable DNA-lipid complexes. Mechanical properties of the films of crosslinked DNA-lipid complexes will be investigated.

Research 3 DFB Laser（Distributed Feedback Laser)

A DFB laser structure by coating laser-dye doped DNA-lipid complexes was fabricated on a patterned PMMA substrate. Lasing threshold of DBASMPI (one of the hemyciannine dye derivatives) doped DNA-CTMA thin film DFB laser was about 1 mJ/cm^2.

INTRODUCTION-

This research proposal describes preparations of innovative photonic devices based on high purity

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14. ABSTRACT

This research proposal describes preparations of innovative photonic devices based on high purity DNA molecules which are obtained from Salmon roe. DNA molecules have characteristic features of double helical chain structures where aromatic compounds can intercalate into the stacked layers so that various optically active aromatic dyes indicate strong enhancement effects of photonic activities. Thus, various DNA photonic devices have been developed in the world in terms of optical switches, electro-luminescence (EL), lasers and so on.1-6) However, these DNA photonic devices adsorb moisture in the air because of hydrophilic character of DNA molecules, leading to decrease photonic activities. Nevertheless, it was reported that a novel hybridization method of the dye-intercalated DNA molecules by means of so-called so-gel process increased stabilities and durability of DNA photonic devices under environmental changes.

15. SUBJECT TERMS

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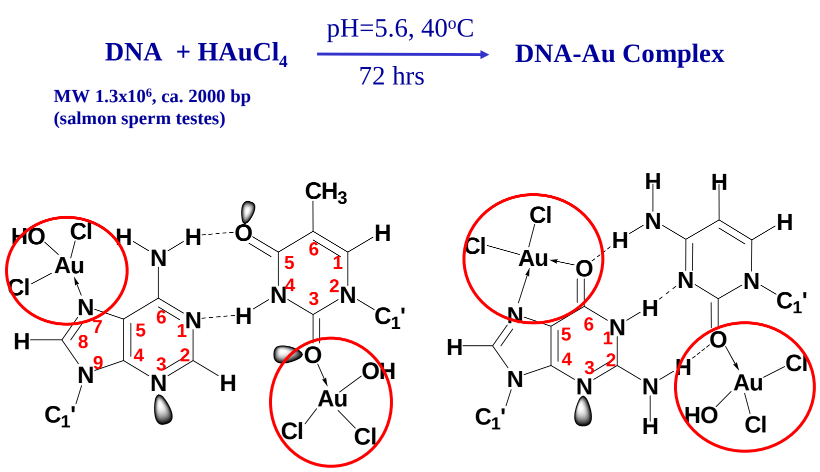
DNA molecules which are obtained from Salmon roe. DNA molecules have characteristic features of double helical chain structures where aromatic compounds can intercalate into the stacked layers so that various optically active aromatic dyes indicate strong enhancement effects of photonic activities. Thus, various DNA photonic devices have been developed in the world in terms of optical switches, electro-luminescence (EL), lasers and so on.[1-6] However, these DNA photonic devices adsorb moisture in the air because of hydrophilic character of DNA molecules, leading to decrease photonic activities. Nevertheless, it was reported by my group that a novel hybridization method of the dye-intercalated DNA molecules by means of so-called so-gel process increased stabilities and durability of DNA photonic devices under environmental changes. Also, hybridization of dye-intercalated DNA devices with synthetic polymers including poly(methylmethacrylate) or polycarbonates was successfully carried out by solution blending method, followed by casting the solution to obtain these films which showed stability and durability increases of these DNA photonic devices.

These research results strongly stimulate further developments of DNA photonic applications to create innovative DNA devices. Photonic or electronic devices are fabricated as thin films which need mechanical stability with less brittleness. Normally, crosslinking reactions of various polymers result in increasing mechanical strength, while they become brittle and fragile. It is required to improve both mechanical strength and elasticity for processing DNA devices. This research proposal aims at developments of innovative DNA photonic devices in terms of discovery of novel crosslinkers of DNA complexes for the increase of mechanical properties and DFB lasing based on DNA films for light transmission.

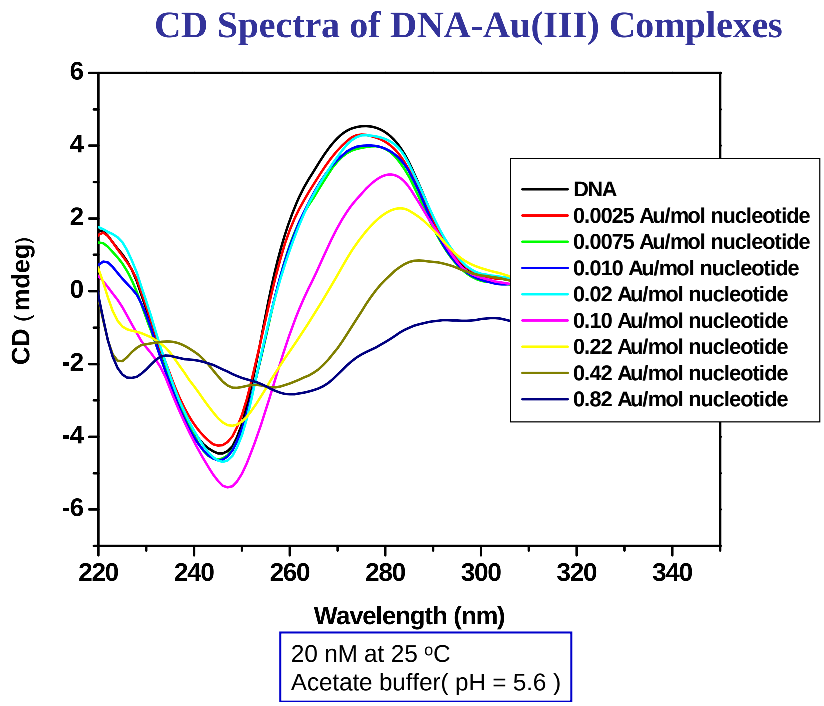
It was reported by Prof. JI.Jin[7] of the Korea University that a chelation occurred when DNA was doped by $HAuCl_4$ as follows:

Preparation of DNA-Au(III) Complexes



adenine-thymine **guanine-cytosine**

The chelation of DNA with Au^{+++} induced to form a single chain DNA which was verified by measuring CD spectra as function of Au^{+++} concentration, as shown in below figure. He described that the chelation of DNA with Au^{+++} cation induced a magnetic property which is very interesting in terms of applications of DNA to electronics such as field effect transistors. Thus, chelation of DNA with novel metal or rare earth metal compounds was investigated in terms of light amplifications.



RESULTS AND DISCUSSON

Research 1 Chelation of DNA with novel metals or rare earth metal compounds.

Prof. Jin[7)] described that the chelation of DNA with Au^{+++} cation induced a magnetic property which is very interesting in terms of applications of DNA to electronics such as filed effect transistors. When Pd^{++} or Eu^{+++} cations were added to DNA aqueous solutions, CD spectra became completely flat as shown in Fig.1, indicating that DNA double helical chain got to loose to a single chain.

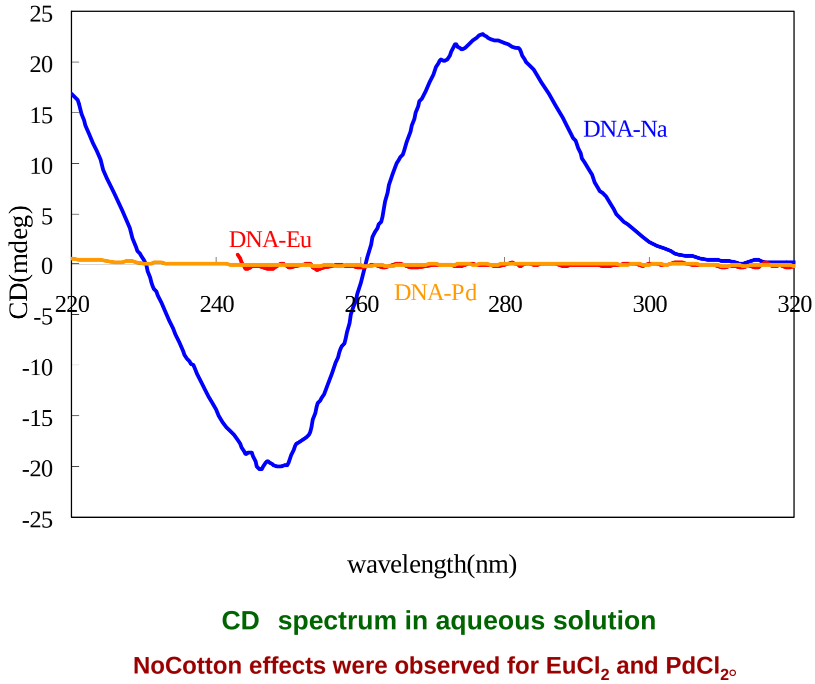
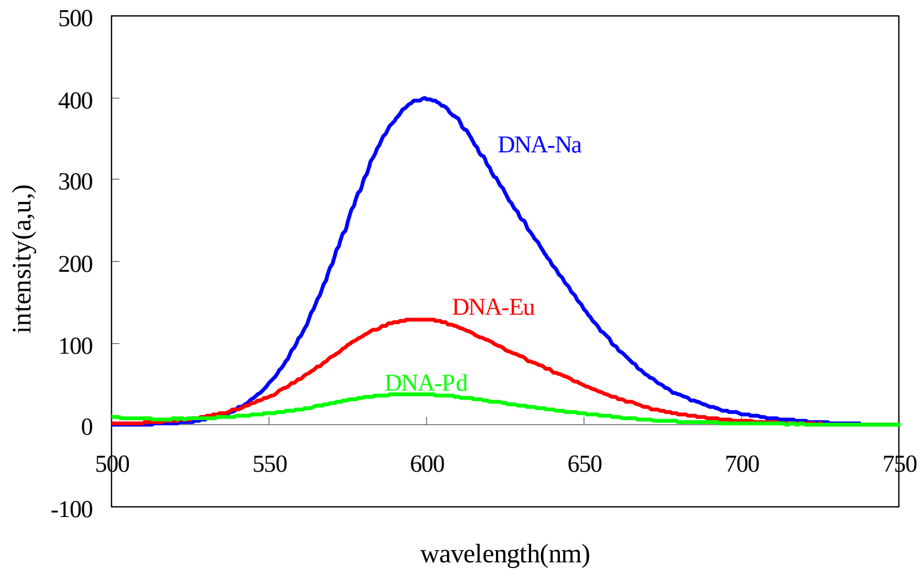


Fig.1 CD spectra of DNA in the presence of Eu^{+++} or Pd^{++}

A single chain formation of DNA could be confirmed by intercalating ethyzium bromide (EtBr)to DNA since fluorescence intensity of EtBr is greatly enhanced by the intercalation of EtBr into the double helical structure of DNA. Fig. 2 indicates fluorescence intensity of EtBr in the presence of Eu^{+++} or Pd^{++} and it is seen in Fig.2 that less fluorescence intensity was observed, indicating a single chain formation of DNA.

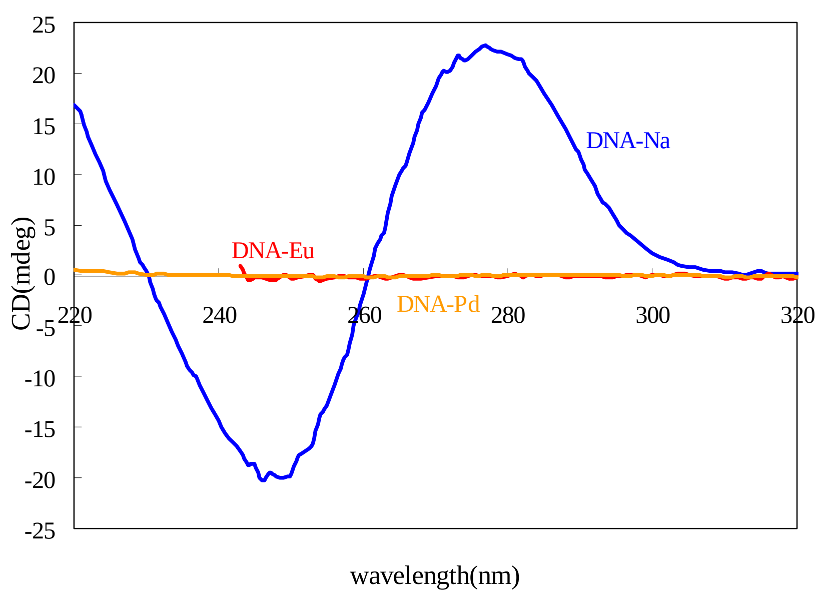


Each concentration: 0. 01wt%、EtBr: 0. 01wt%

Large decreases in fluorescence intensity. No intercaltion of EtBr in DNA

Fig. 2. Fluorescence intensity of DNA in the presence of Eu^{+++} or Pd^{++}

When Pd^{++} or Eu^{+++} cations were added to DNA aqueous solutions, CD spectra became completely flat as shown in Fig.3, indicating that DNA double helical chain got to loose to a single chain.

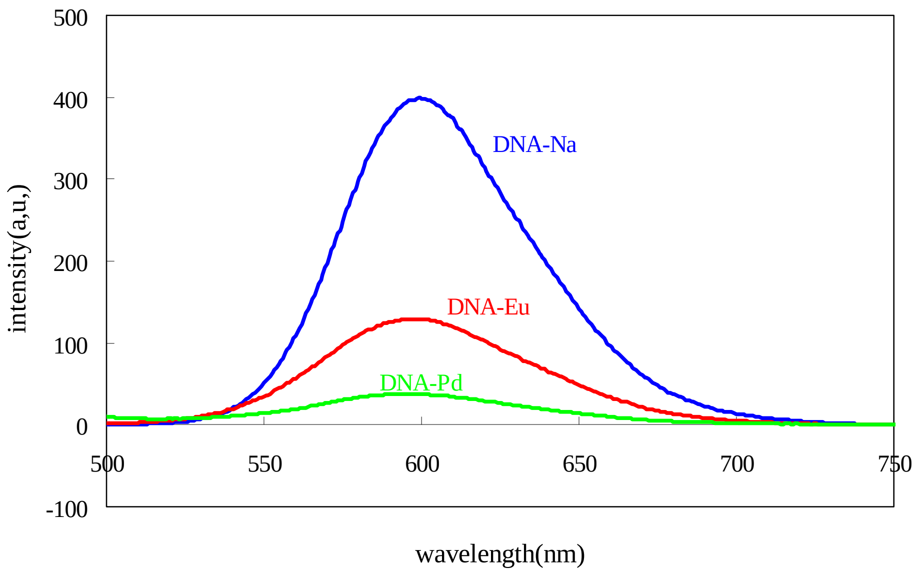


CD spectrum in aqueous solution

NoCotton effects were observed for $EuCl_2$ and $PdCl_2$。

Fig.3 CD spectra of DNA-Pd^{++} or DNA-Eu^{+++}

A single chain formation of DNA could be confirmed by intercalating ethyzium bromide (EtBr)to DNA since fluorescence intensity of EtBr is greatly enhanced by the intercalation of EtBr into the double helical structure of DNA. Fig. 4 indicates fluorescence intensity of EtBr in the presence of Eu^{+++} or Pd^{++} and it is seen in Fig.4 that less frescence intensity was observed, indicating a single chain formation of DNA.

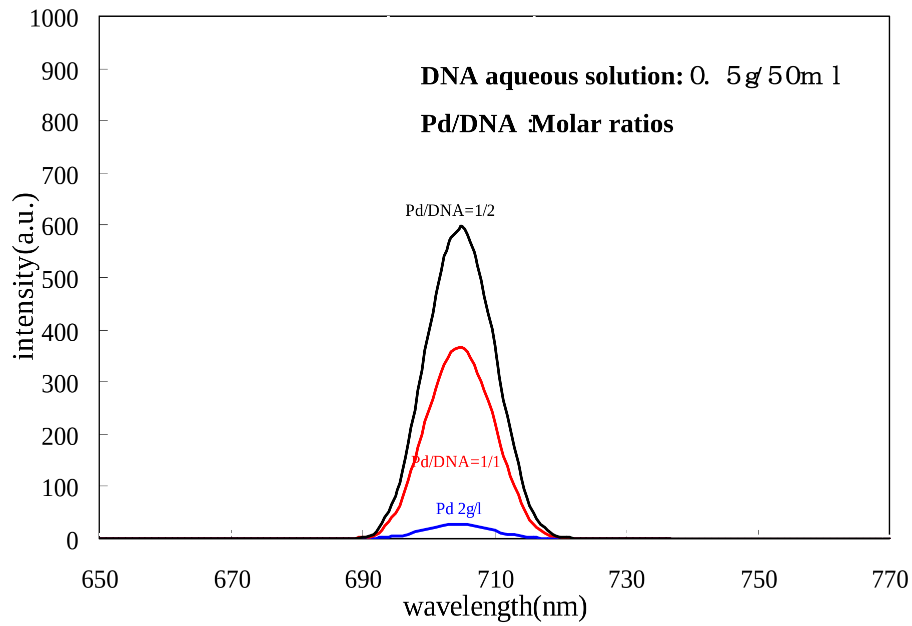


Each concentration: ０．０１ｗｔ％、**EtBr:** ０．０１ｗｔ％

Large decreases in fluorescence intensity. No intercaltion of EtBr in DNA

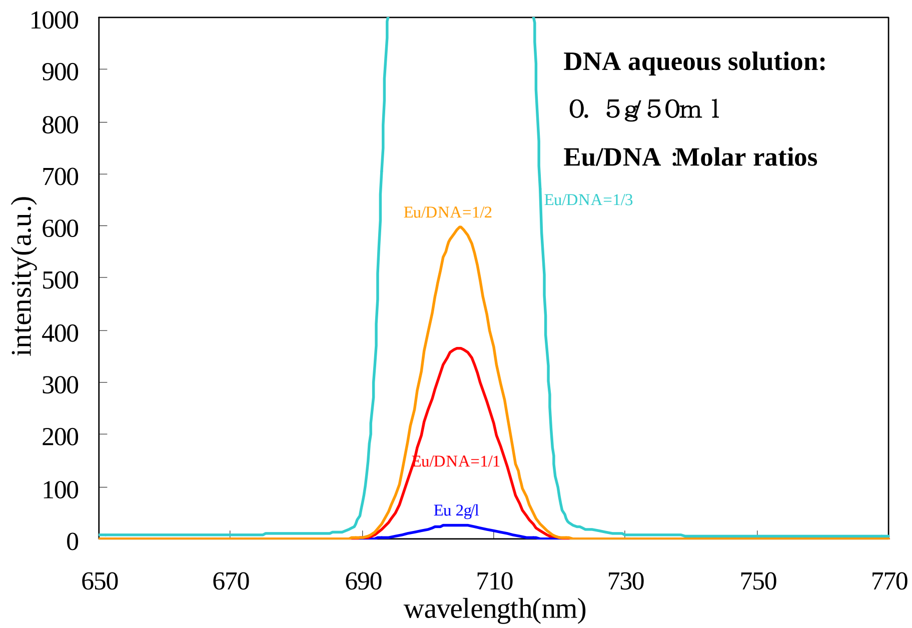
Fig. 4 Fluorescence intensity of DNA in the presence of Eu^{+++} or Pd^{++}

Fluorescence intensity of aqueous solution of DNA in the presence of Pd^{++}, Eu^{+++}. Tb^{+++} and Nd^{+++} was measured and results are summarized in Figs.5-8, respectively. These figures indicate large amplifications of fluorescence light in the presence of novel metal or rare earth metal cations, especially Eu^{+++} or Tb^{+++} showed a very large fluorescence emission with increasing amount of DNA. Fig. 9 shows effects of DNA ratios to rare earth metal cations, which indicates a large fluorescence emission occurred with increasing ratios of DNA to rare earth metal cations. especially in the rage of more than 2 of DNA to Eu^{+++} or Tb^{+++}. These results strongly suggest that electron shells would be twisted and electron state including electron spin would be changed by interactions with nucleic acid bases of DNA. These results suggest that the DNA magnet would be possible as Prof. Jin suggested. Novel electronic applications of DNA will be open by these results and further research on DNA electronics is required.



Fluorescence spectrum of aqueous solutions of DNA-$PdCl_2$

Fig 5 Fluorescence intensity of DNA/Pd^{++} solution with increasing ratios of Pd^{++}



Fluorescence spectrum of DNA-$EuCl_2$ in aqueous solution

Fig 6 Fluorescence intensity of DNA/Eu^{+++} solution with increasing ratios of Eu^{+++}

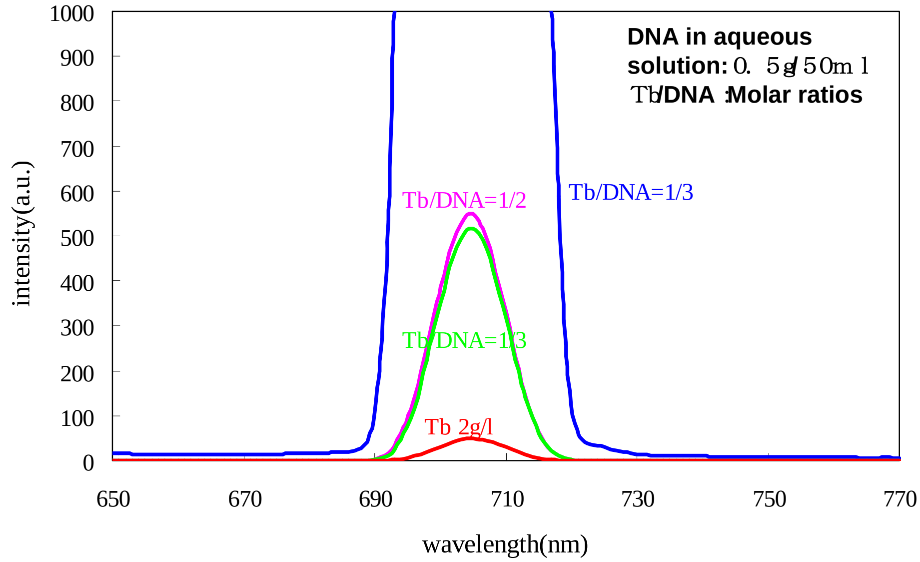
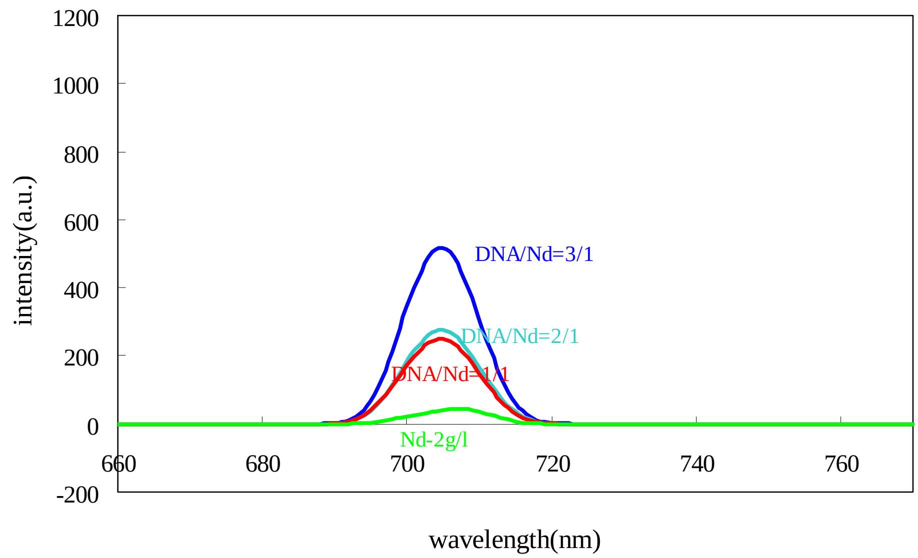


Fig 7 Fluorescence intensity of DNA/Tb^{+++} solution with increasing ratios of Tb^{+++}



DNA concentration: 0.01g/50ml

Fig 8 Fluorescence intensity of DNA/Nd^{+++} solution with increasing ratios of Nd^{+++}

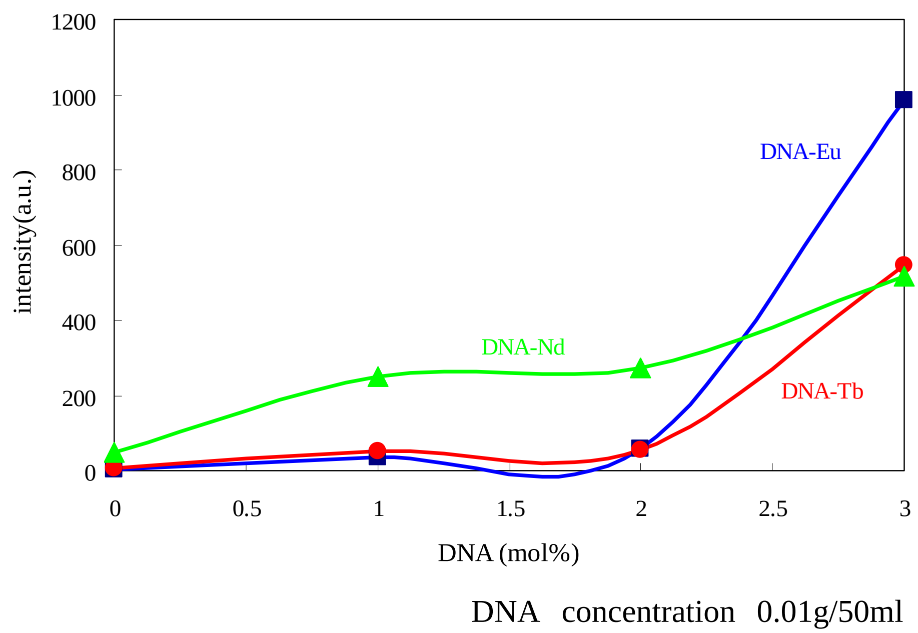


Fig.9 . Fluorescence intensity as functions of DNA ratios

Research 2. Novel crosslinkers of DNA devices to improve mechanical strength

Photo-crosslinking reactions of DNA-CTMA complex under UV irradiation will be carried out in terms of the effect of various UV photo-initiating agents. DNA molecules are known to cause a crosslinking reaction under UV irradiations which is explained as a dimerization among thymine groups in DNA. However, the crosslinking reactions of DNA result in transformation of double helical structures of DNA molecules leading to random conformations of DNA molecules, which may lead to reduce an elasticity of DNA films to increase brittleness. Fabrications for processing DNA devices require to avoid brittleness and cracking of the DNA films.

DNA-lipid complexes consist of double capsular structures of outside layers of lipid groups and inside zones of double helical DNA molecules. When a powerful radical initiators under UV irradiation is used, radical groups are produced within outside lipid molecules, resulting in crosslinking reactions of the DNA-lipid molecules which may still keep the double helical structures of DNA molecules. Thus, the crosslinking reactions may not cause the decrease of elasticity of DNA films. Number of powerful radial initiators for living polymerization will be used to initiate the crosslinking reactions of outside lipid layers to keep the mechanical strength as well as elasticity.

UV curable lipids can be synthesized for the DNA-lipid complexes to initiate the photo-crosslinking reactions of the DNA-lipid complexes keeping the double helical structures of DNA molecules. Various UV curable lipids containing acrylate group can be synthesized by starting choline and acrylate-containing acids as shown in following chemical equation:

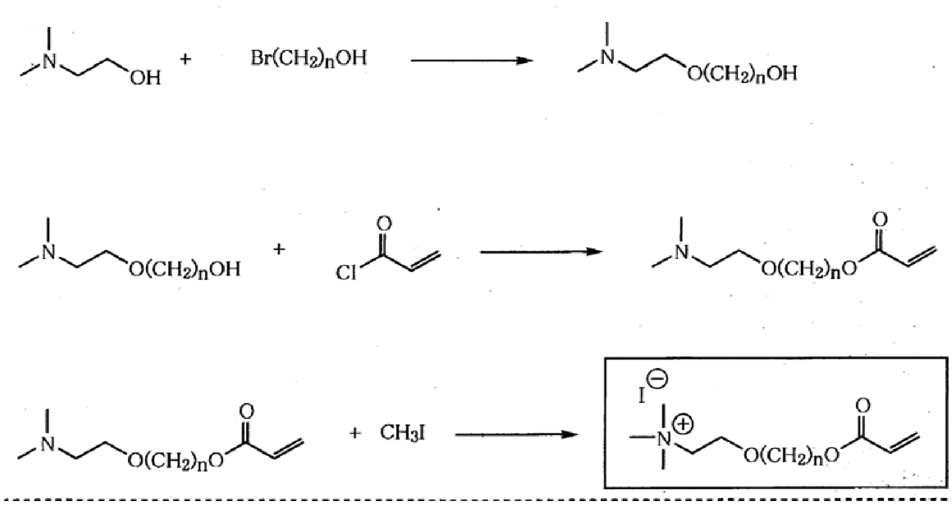
$$(CH_3)_3N^+CH_2CH_2OH + HOOC\text{-}R\text{-}OCOCH{=}CH_2 \longrightarrow$$

Choline

$$(CH_3)_3N^+CH_2CH_2OCO\text{-}R\text{-}OCOCH{=}CH_2$$

At first, γ–hydoxycaproic acid was reacted with acryloyl chloride to prepare γ–acryloxy caproic acid $CH_2{=}CHCOO(CH_2)_5COOH$ (ACA), followed by the esterification of choline in the presence of condensation agents such as DCC(dicyclohexylcarbodimide) under mild conditions at ambient temperature. However, the esterification reaction did not successfully occur since the esterification reaction proceeds through an interface between water containing choline and organic solvents containing ACA. After several failures of the synthetic reaction, following reaction route was selected:

Synthetic route for choline lipids



The synthesis to prepare the choline-derived lipids is being carried out , followed by the preparation of DNA-lipids containing UV curable acrylate group.

Research 3. DFB Laser（Distributed Feedback Laser)

DFB laser is very important to transmit light information through optical cables because of avoiding much less contaminations of various noises through optical cables. It was reported by my group that optical dye-intercalated DNA indicated a strong lasing effect of fluorescence light by irradiating UV light. Fine regulated patters of dye-intercalated DNA films are expected to create novel innovative DFB film laser. Pattering of dye-intercalated DNA film will be carried out to make a DFB laser and the lasing effect will be investigated. Following research targets is focused:

1. DFB laser structure by coating laser-dye doped DNA-lipid complexes onto a etchless-grating fabricated on PMMA substrate.
2. Selections of various laser dyes such as DBASMPI (one of the hemycianine dye derivatives) for less lasing threshold values of doped DNA-CTMA thin film DFB laser
3. Structural surface analyses of patterned DNA films by AFM for sophisticated device structure.

Fig. 10 shows a fabrication process to prepare the etchless grating on a PMMA substrate. An original pattern was exposed on a photoresist surface which was coated on a glass substrate by a two-beam interference of a Hd-Cd laser. After developmet and rinse processes of the photoresist, the formed pattern was transferred to a PMMA substrate by pressing the original pattern on the photoresist with organic solvent such as dicholoromethane

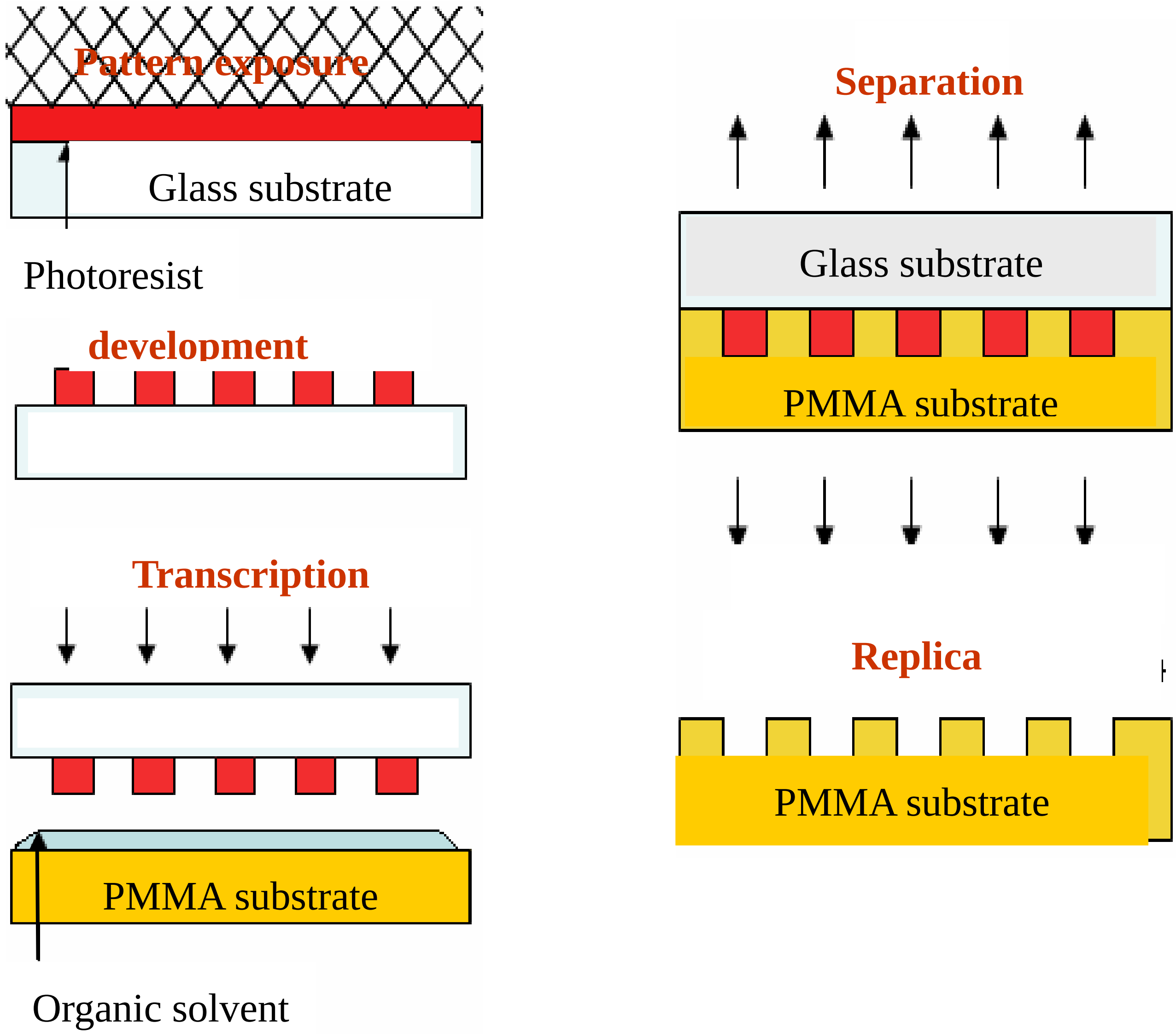


Fig. 10 Fabrication processes of patterned PMMA substrate

Fig.11 shows a patterned PMMA substrate which was observed by a scanning electron microscopic (SEM) and an atomic force microscopic (AFM) pictures. Line widths of these patterns were approximately 1μm.

Then,DNA-CTMA containibng 1wt% of a dye was overcoated on the patterned PMMA substrate by using a spin-coating method of 1wt% ethanol-chororoform (!/4) solution of DNA-CTMA-laser-dye: 4-[4-(Dibutyl amino)styryl]-1-metyl pyridinium iodide(DBAMSPI), as shown in Fig. 12.

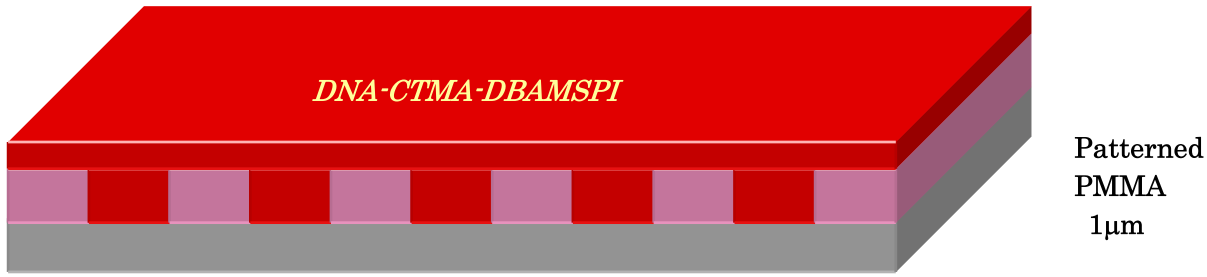


Fig. 12 Overcoaing of DNA-CTMA-dye layer on a patterned PMMA

An experimental setup to measure laser emission is shown in Fig. 13 and a result of the laser emission is shown in Fig. 14, which indicates a sharp laser light emission from the DNA film.

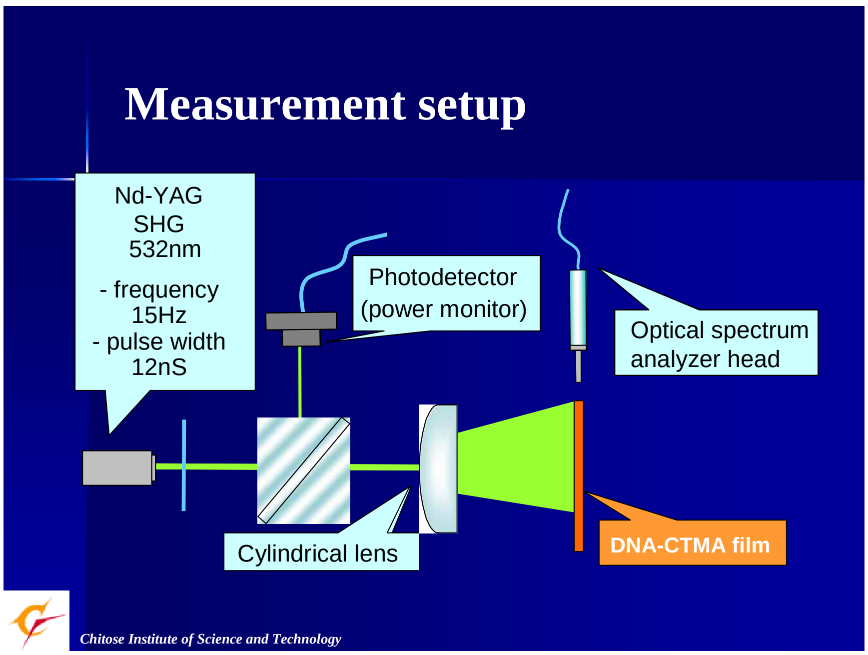


Fig. 13 Experimental setup to measure lasing emission

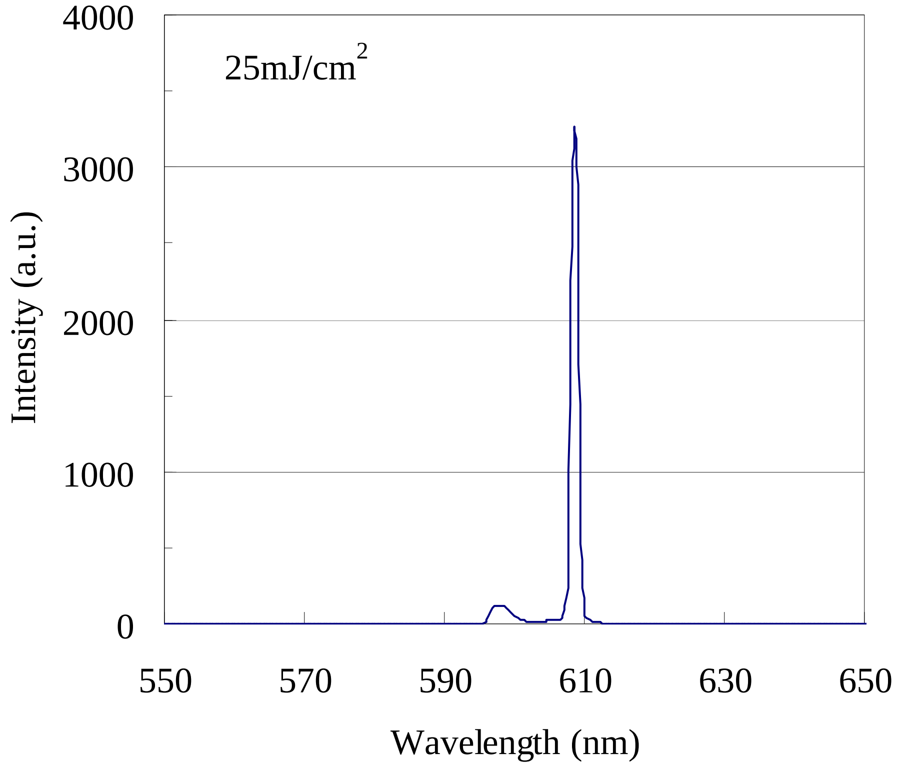


Fig. 14 Laser emission from the DNA-CTMA-DBASMPI film

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Thus, a DFB laser structure by coating laser-dye doped DNA-lipid complexes onto a etchless-grating was fabricated on PMMA substrate and a lasing occurred by irradiating the DNA film. Lasing threshold of DBASMPI (one of the hemyciannine dye derivatives) doped DNA-CTMA thin film DFB laser was about 1 mJ/cm^2.

4. CONCLUSIONS

Research 1 Chelation of DNA with novel metals or rare earth metal compounds.

Large amplifications of fluorescence light were attained in the presence of novel metal or rare earth metal cations, especially Eu^{+++} or Tb^{+++} showed a very large fluorescence emission with increasing amount of DNA. These results strongly suggest that electron shells would be twisted and electron state including electron spin would be changed by interactions with nucleic acid bases of DNA. Novel electronic applications of DNA will be open by these results and further research on DNA electronics is required.

Research 2 Novel crosslinkers of DNA devices to improve mechanical strength

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Research 3 DFB Laser（Distributed Feedback Laser)

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5. REFERENCES

1. L. Wang, J. Yoshida, N. Ogata, S. Sasaki and T. Kamiyama: “Self-assembled supramolecular films derived from marine deoxyribonucleic acid (DNA) – cationic lipid complexes: large-scale preparation and optical and thermal properties”, *Chem. Mater.*, **13,** 1273-1281, 2001.
2. J. Yoshida, L. Wang, S. Kobayashi, G. Zhang, H. Ikeda and N. Ogata: “Optical properties of photochromic-compound-doped marine-biopolymer DNA-lipid complex films for switching applications”, *Proc. SPIE*, **5351,** 260-268, 2004.
3. W. M. Heckman, J. Grote, P. P. Yaney and F. K. Hopkins: “DNA-based nonlinear photonic materials”, *Proc. SPIE*, **5516,** 47-51, 2004.
4. P. P. Yaney, E. M. Heckman, D. E. Diggs, F. K. Hopkins and J. Grote: “Development of chemical sensors using polymer optical waveguides fabricated with DNA”, *Proc. SPIE*, **5724,** 224-233, 2005.
5. A. Watanuki, J. Yoshida, S. Kobayashi, H. Ikeda and N. Ogata: “Optical and photochromic properties of spiropyran-doped marine-biopolymer DNA-lipid complex films for switching applications”, *Proc. SPIE*, **5724,** 234-241, 2005.
6. J. Yoshida, A. Watanuki, S. Kobayashi, H. Ikeda and N. Ogata: “Potential switching application based on the photochromism of spiropyran-doped marine-biopolymer DNA-lipid complex films”, *Tech. Digest*, *10th Optoelectronics and Communication Conference (OECC2005)*, 342-343, 2005, Seoul, Korea.
7. Y-W.Kwon, C.H.Lee, D-H.Choi, and J-I Jin, ”Material Chemistry of DNA”, *J. Mat. Chem.*, **19,** 1353-1380(2009)

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