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DNA Photonics [Deoxyribonucleic Acid]

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Purified deoxyribonucleic acid (DNA) derived from salmon and scallop sperm has demonstrated excellent passive and active optical properties. Characterization of the optical and electromagnetic properties of DNA suggests suitability for photonic applications. One of interesting features of DNA we discovered was an intercalation of aromatic compounds into stacked layers within the double helix of DNA molecules. We found that various optical dyes inserted into the double helix of DNA molecules rendered active optical waveguide materials with excellent nonlinear optical properties. Our research included the investigation of DNA for use as an optical waveguide material as well as intercalation of fluorescent dyes, photochromic dyes, nonlinear optic chromophores, two photon dyes and rare earth compounds into DNA for use as a nonlinear optical material.

Keywords: cladding; conductive polymer; deoxyribonucleic acid; DNA; electro-optic modulator; fluorescence; nonlinear; optical amplifier; waveguide

INTRODUCTION

Investigation of nonlinear optic materials for electro-optic waveguide devices, optical memory and optical amplifier applications has led us to a promising material, marine based deoxyribonucleic acid (DNA). It is derived from waste material from the salmon fishing industry and is, therefore, abundant and affordable. It is also a green material. Preliminary investigations have suggested that DNA shows promise to be a more suitable optical material than many of the polymers currently being used for photonic waveguides and devices.

Marine DNA used for this investigation was purified at the Chitose Institute of Science and Technology (CIST) [1,2]. The DNA was first isolated from frozen salmon sperm through a homogenization process. It then went through an enzymatic treatment to degrade the proteins by protease. Proteins were then removed by controlling the pH level to 7.5. The DNA underwent a carbon treatment for decolorization, was filtered, and precipitated by adding acetone. The purified DNA was finally filtered from the acetone and freeze dried. See Figure. 1. The molecular weight of the purified DNA measured $M_W = 500,000-6,500,000$, the purity measured Assay $= 96\%$ and the protein content measured 2%.

We found, however, that the purified DNA dissolved only in water. It did not dissolve in any of the organic solvent typically used for the fabrication of polymer based photonic devices. In addition the DNA films produced were not of high enough optical quality for photonic waveguide applications. Therefore, we performed additional processing to render DNA more suitable for device fabrication with better optical quality.

FIGURE 1 Freeze dried, purified salmon DNA.

This processing was accomplished by precipitating the purified DNA in water with a cationic surfactant complex, hexadecyltrimethylammonium chloride (CTMA), by an ion exchange reaction [1,3]. This replaced the sodium cation of the DNA. See Figure 2. This was done at both CIST and the Air Force Research Laboratory (AFRL). The resulting DNA-lipid complex became water insoluble and more mechanically stable due to the long alkyl chain of the CTMA.

Adding the CTMA complex, DNA-CTMA could now be dissolved using solvents more compatible with device fabrication, such as chloroform, ethanol, methanol, butanol or a chloroform/alcohol blend. When dissolved in the organic solvent the DNA-CTMA was passed through a 0.2 μm filter to remove any large particulates [3].

Thin films of DNA-CTMA were then cast and spin deposit onto substrates and its optical and electromagnetic properties were characterized.

EXPERIMENT

The ratio of DNA-CTMA to solvent we used was 1:10. Butanol was the preferred solvent for spin depositing because of its higher boiling point. Chloroform was the preferred solvent for casting films because of its lower boiling point.

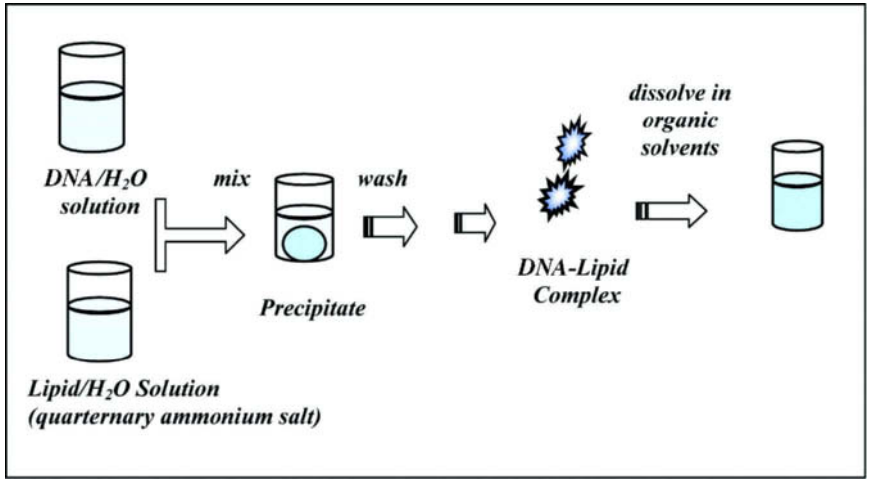


FIGURE 2 Procedure for preparation of DNA-CTMA complex.

We spin deposited the filtered DNA-CMA complex onto various substrates such as uncoated glass slides, 50 nm indium tin oxide coated glass slides and SiO_2 coated Si substrates, at 800 rpm for 10 sec. and baked the samples at 120°C for 60 min. This produced very uniform 3 μm thick films.

We also cast thicker films of DNA-CTMA to characterize the optical absorption and loss. These cast films measured 300 μm thick.

To evaluate DNA-CTMA's potential as an optical waveguide material, the refractive index of DNA-CTMA was measured as a function of wavelength, the optical absorption and loss were measured as a function of wavelength, the resistivity was measured as a function of temperature, the dielectric constant was measured as a function of frequency. In addition, we tested the material's temperature stability and it's resistance to various organic solvents used for polymer waveguide fabrication.

With favorable results, which are presented in the results, we began adding various nonlinear optical dyes to the DNA-CTMA complex to evaluate intercalation, material compatibility and material characteristics. See Figure 3. These dyes included fluorescent dye 4-[4-(dimethylamino)stylyl]-1-dococylpyridinium bromide (DMASDPB), photochromic dye spiropyran, rare earth metal compound Eu-FOD, NLO chromophores disperse red 1 (DR1) and Cheng Larry Dalton 1 (CLD1), and two photon dye 1433. See Figure 4. Results of this initial study are presented in the next section.

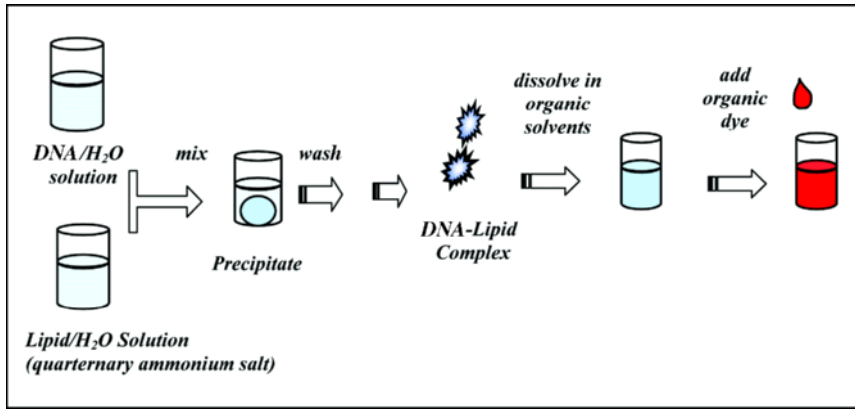


FIGURE 3 Procedure for preparation of organic dye/DNA-CTMA blend.

RESULTS AND DISCUSSION

We first tested the DNA-CTMA film's resistance to cyclopentanone, dichloroethane, toluene and tetrahydrofuran. These are typical solvents used for polymer based optical waveguide materials. We found that these solvents had no visible effects on the DNA-CTMA film, indicating good resistance to these types of solvents [3].

We measured the optical transmissivity of a 3 μm thick DNA-CTMA film using a Cary spectrophotometer. Figure 5 is a plot of the spectrophotometer data [3]. As can be seen in Figure 5, the DNA-CTMA film exhibits excellent transmissivity over a broad wavelength range. We then measured the absorption spectrum of a 300 μm thick film of DNA-CTMA using a Cary Spectrophotometer. The data recorded in Figure 6 identifies DNA-CTMA as a very low loss optical material applicable over a broad range of wavelengths.

We measured the refractive index of the DNA-CTMA thin film as a function of wavelength. The refractive index range was from 1.540–1.526. See Figure 7.

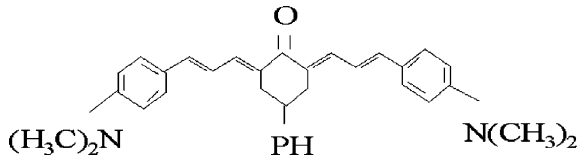


FIGURE 4 Two photon dye-Sample 1433.

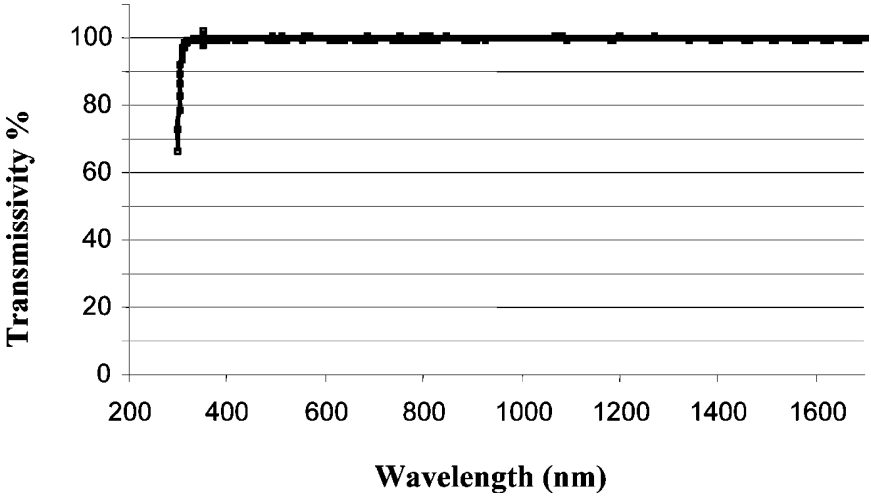


FIGURE 5 Transmissivity of a 3 μm thick DNA-CTMA thin film.

Figure 8 is an end view image of planar optical waveguiding at $\lambda = 633$ nm through a 3 μm thick DNA-CTMA film spin deposited on a SiO_2 coated silicon substrate using a cylindrical lens which collimated the laser in the horizontal direction [3,4].

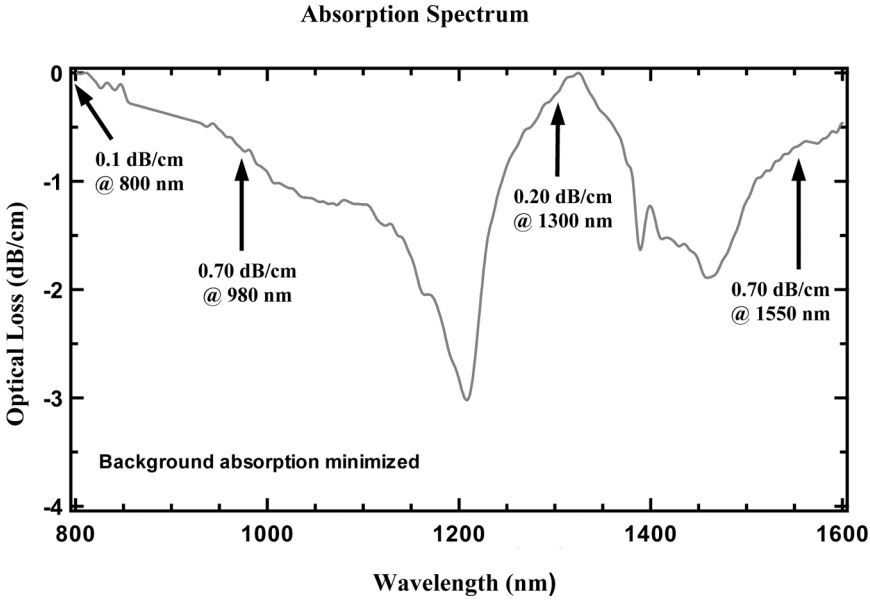


FIGURE 6 Absorption spectrum of 300 μm thick film of DNA-CTMA.

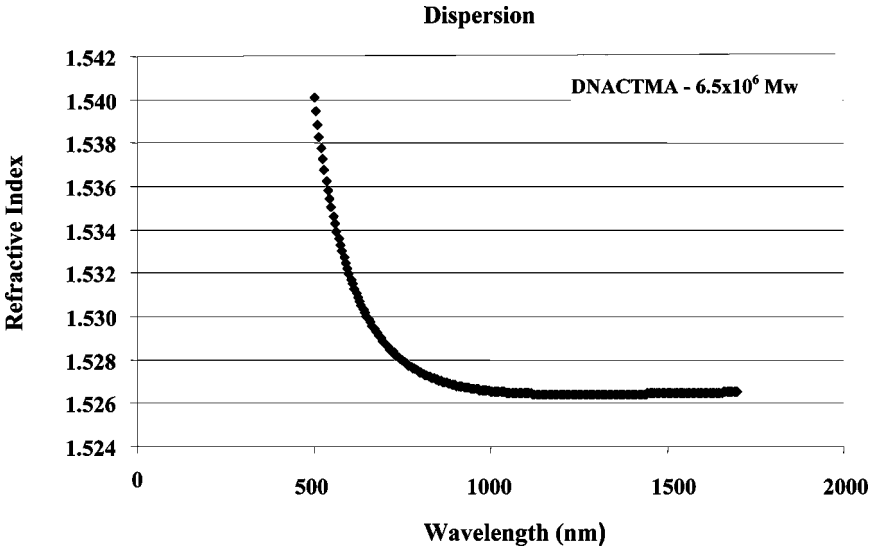


FIGURE 7 Refractive index of DNA-CTMA.

The resistivity of 3 μm thick DNA-CTMA films with molecular weights of 500,000 and 6,500,000 were measured as a function of temperature. The data in Figure 9 suggests that the resistivity of DNA-CTMA might be adjusted by controlling the molecular weight.

Figure 10 is a plot of the dielectric constant of DNA-CTMA versus frequency. These were measured in air at low frequencies [3].

Finally we performed a thermo-galvometric analysis (TGA) of the DNA-CTMA complex which showed material stability up to 230°C and 10% water absorption in air at room temperature. See Figure 11.

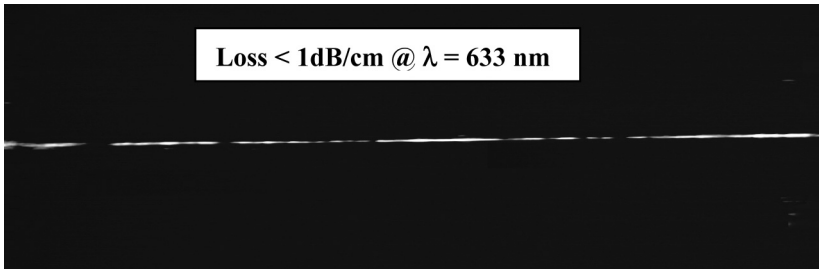


FIGURE 8 End view of waveguiding through a 3 μm thick DNA-CTMA thin film.

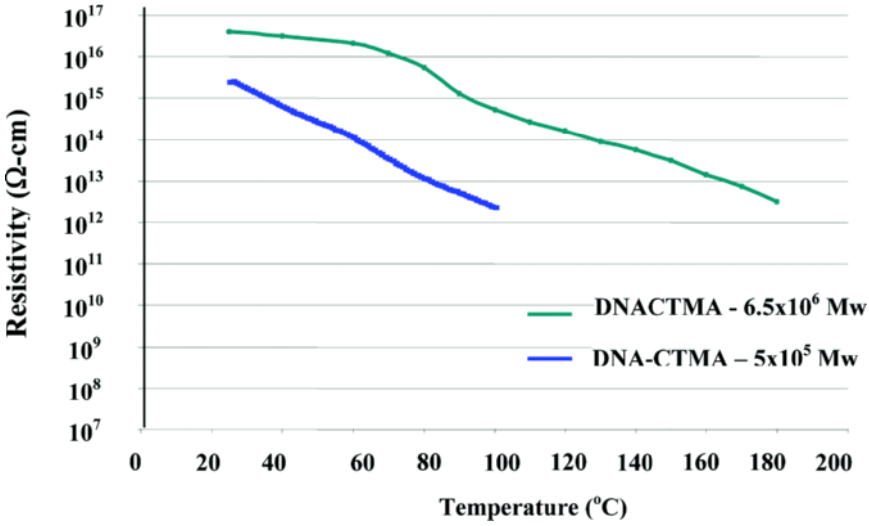


FIGURE 9 Resistivity vs. temperature for DNA-CTMA complexes.

Table 1 gives a summary of the preliminary measurements of the properties of DNA-CTMA complex. These results are very encouraging. They suggest that DNA-CTMA may be a good potential photonic waveguide material.

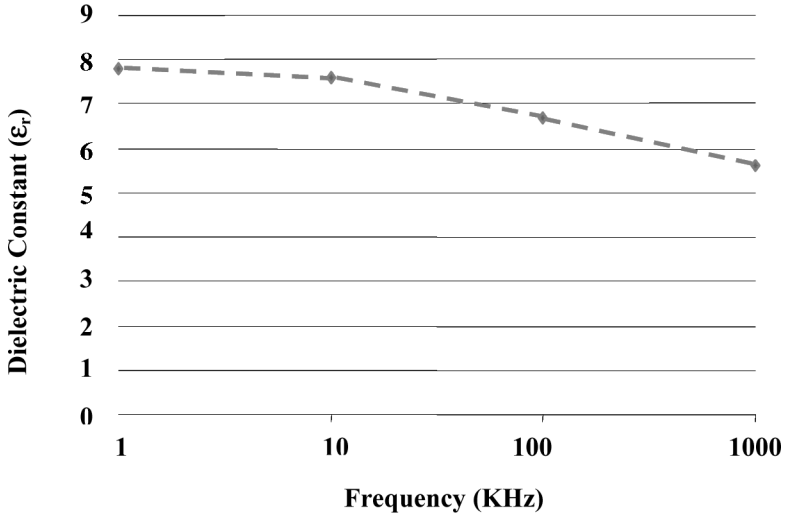


FIGURE 10 Dielectric constant versus frequency for DNA-CTMA complex.

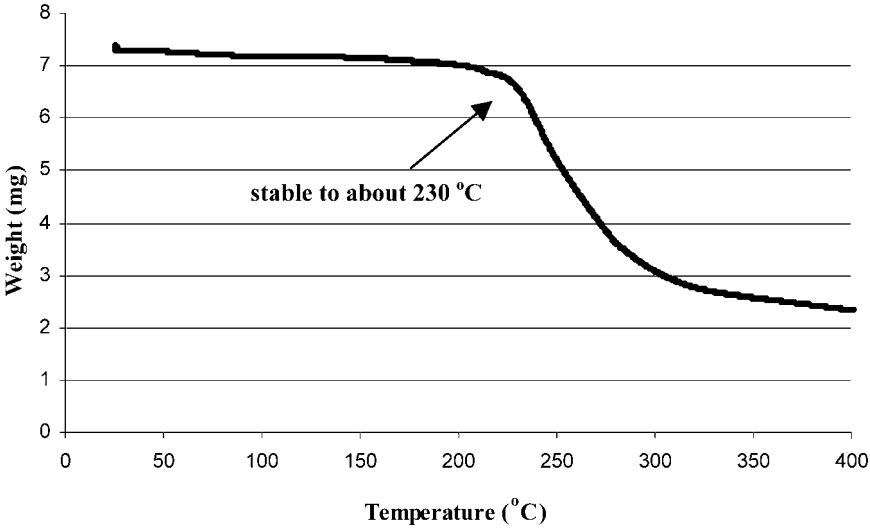


FIGURE 11 Thermo-galvometric analysis (TGA) of DNA-CTMA material.

We first explored its use as an optical cladding material for NLO polymer based EO modulators [3]. Poling experiments were conducted using DNA-CTMA as a cladding layer and both DR1-PMMA and CLD1-PMMA as the NLO polymer core materials [3–8]. See Figure 12.

The films were spin deposited. We electrode poled both the control sample and cladding sample using the same parameters. The poling temperature was set at 80°C, and the poling field was set at 80 V/μm. The EO coefficient was measured using the Teng and Mann technique [9]. Table 2 contains the results of this experiment.

TABLE 1 Summary of Properties of DNA-CTMA

- n = 1.526 – 1.540
- Resistivity ρ(DNA) =< $10^{-2}\cdot\rho$(CLDI/APC)
- Transmissivity ~ 100% , $\lambda = 350 - 1700$ nm
- Propagation loss ≤ 1 dB/cm λ = Broad
- Dielectric constant εr(DNA) = 7.8@ 1 KHz, 5.6@1 MHz
- Temperature cured
- Stable to 230°C (TGA)
- Water insoluble
- Ethanol, Methanol, Butanol, Chloroform Solvents
- Does not dissolve PMMA or APC (Alcohol based solvents)
- Resistant to Cyclopentanone, Dichloroethane, Toluene, Tetrahydrofuran (THF) and aqueous solutions
- ~10% Water absorption @ Room temperature

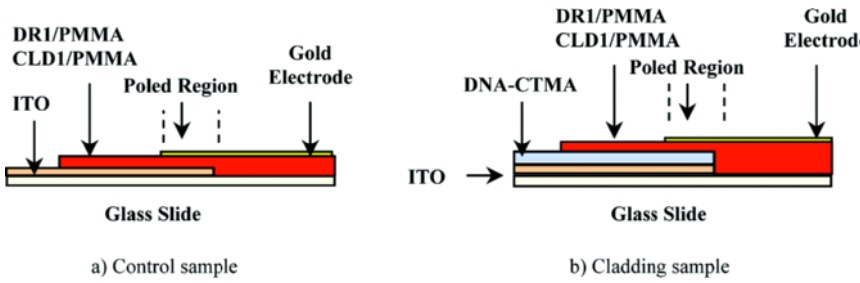


FIGURE 12 Poling experiments.

The calculated values for the EO coefficient using the DNA-CTMA cladding layer were 7% and 15% less than the measured values for the DR1 in PMMA and CLD1 in PMMA cores, respectively, suggesting that the poling efficiency was m $>90\%$ using a DNA-CTMA cladding layer [3]. High poling efficiency, along with the anticipated optical propagation loss, and with resistance to the type of solvents used for NLO polymers, render DNA-CTMA an excellent candidate for a bottom cladding material for NLO polymer devices. In addition, the fact that the alcohol solvents used for DNA-CTMA do not dissolve the typical NLO polymer materials suggests that DNA-CTMA may prove an excellent candidate for a top cladding material as well.

We next began to add nonlinear dyes to the DNA-CTMA [2,4]. We blended DMASDPB dye to DNA-CTMA using an ethanol solvent, cast thin films and measured the fluorescence as a function of dye

TABLE 2 Electro-Optic Coefficient Using DNA-CTMA Cladding Layer

Sample	r_{33} (Measured)	r_{33} (Calculated)
1.8 μm thick	4.6 pm/V	
10 wt% DR1 in PMMA	(±10%)	
No cladding	($\lambda = 633$ nm)	
1.7 μm thick	3.7 pm/V	3.5 pm/V
10 wt% DRI in PMMA	(±10%)	(±10%)
1 μm thick DNA-CTMA	($\lambda = 633$ nm)	($\lambda = 633$ nm)
1.7 μm thick	4.9 pm/V	
10 wt% CLD1 in PMMA	+10%	
No cladding	($\lambda = 1550$ nm)	
1.7 μm thick	4.3 pm/V	3.6 pm/V
10 wt% CLD1 in PMMA	+10%	+10%
1 μm thick DNA-CTMA	($\lambda = 1550$ nm)	($\lambda = 1550$ nm)

concentration. See Figure 13. One can see in Figure 13 that the maximum fluorescence was achieved for 1.8% DMASDPB in DNA-CTMA. This corresponds to the 1:56 ratio in Figure 13. We also compared these results to a sample with 1.8% DMASDPB in PMMA and found that in solution the fluorescence for both samples was comparable. However, after casting films, the fluorescence measured two orders of magnitude higher for DMASDPB in DNA-CTMA. See Figure 14.

Spiropyran-intercalated DNA-CTMA films were cast using an ethanol solvent and their photochromic responses were measured [2,4]. They exhibited a rapid response toward an irradiation by UV light, which we found could be repeated many times. We tested repeatability for 300 cycles. See Figure 15. This suggests that novel DNA based optical memory films might be possible.

A two photon dye, sample 1433, being developed for cancer detection, optical limiting and optical memory (see Fig. 4), was blended with DNA-CTMA using a 2:1 chloroform:butanol solvent mixture.[4] 1% dye in DNA-CTMA film was spin deposited and excited using 1064 nm laser with a 100 mJ pulse energy, a 5 ns pulse length, at a 5 Hz repetition rate. Two photon excitation was observed, but not quantified. See Figure 16.

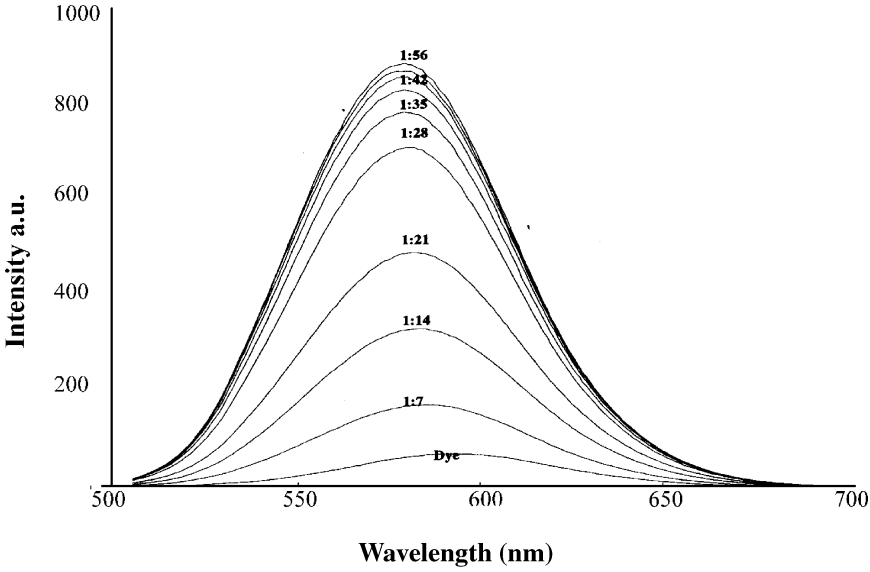
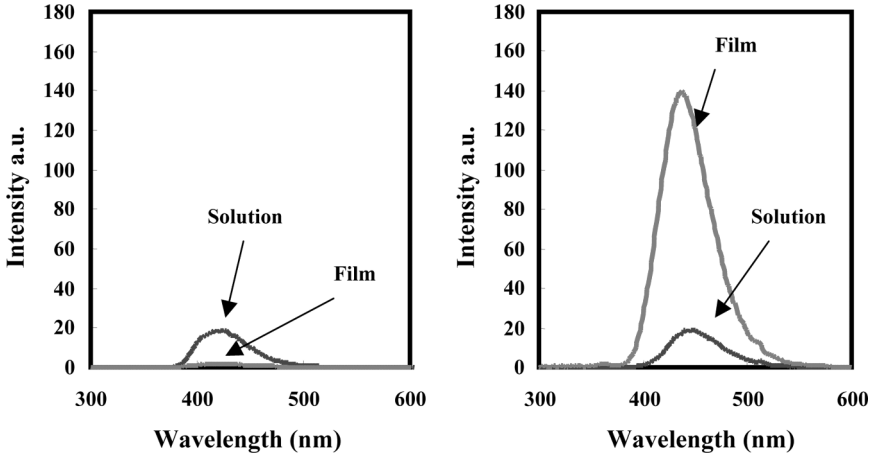


FIGURE 13 Fluorescence versus wavelength for various ratios of DMASDPB in DNA-CTMA.



a) 1.8% DMASDPB in PMMA b) 1.8% DMASDPB in DNA-CTMA

FIGURE 14 Fluorescence vs. wavelength.

NLO chromophores disperse red 1 (DR1) and Cheng Larry Dalton 1 (CLD1) were mixed with DNA-CTMA using a 2:1 chloroform:butanol solvent blend [4]. The samples were spin deposited on indium tin oxide (ITO) coated glass slides producing 5 μm thick films. The chromophore concentration used was 10% for both DR1 and CLD1. The samples were electrode poled at 50°C with an applied electric field of 54 V/μm. We achieved an EO coefficient of 2.13 pm/V at $\lambda = 633$ nm for the DR1 in DNA-CTMA sample. This is comparable to EO coefficient of DR1 in PMMA films with the same concentration of DR1, and under the same

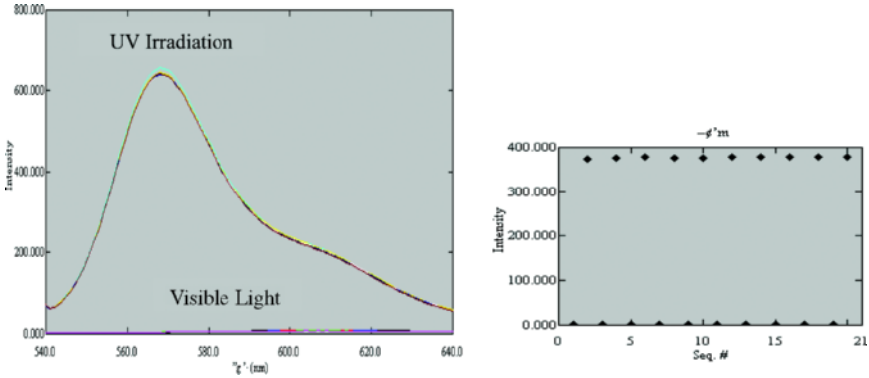


FIGURE 15 Potential for erasable memory films using spiropyran-intercalated DNA-CTMA films.

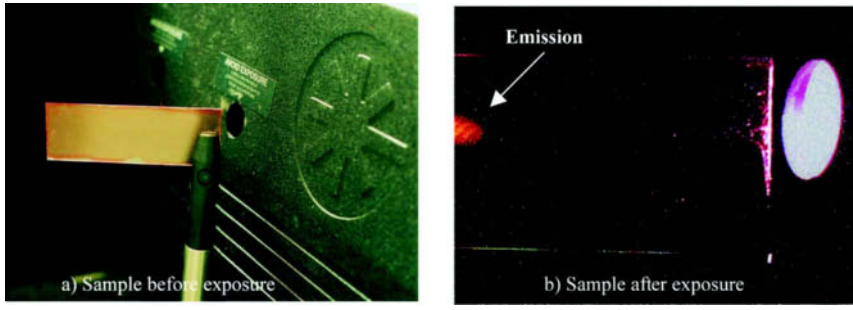


FIGURE 16 1% two photon dye 1433 in DNA-CTMA.

poling parameters [5–8]. We were unable to record data for the CLD1 in DNA-CTMA samples. This may be due to the size of the chromophore in relation to the spacing of the double helix of the DNA-CTMA structure. Further investigation is planned.

The rare earth metal compound europium (Eu) was found to form a stable and strong chelation with the DNA-CTMA complex [2,4]. Thin films of Eu-FOD in DNA-CTMA were cast using an ethanol solvent. These samples exhibited strong amplification of fluorescence at 614 nm, when irradiated with UV light. The amplification we achieved for the Eu-FOD in DNA-CTMA film was more than 100 times that of comparable Eu-FOD dissolved PMMA films. In addition, relaxation times of the fluorescence of the Eu-FOD in DNA-CTMA films were twice as long as those for Eu-FOD in PMMA films. See Figure 17.

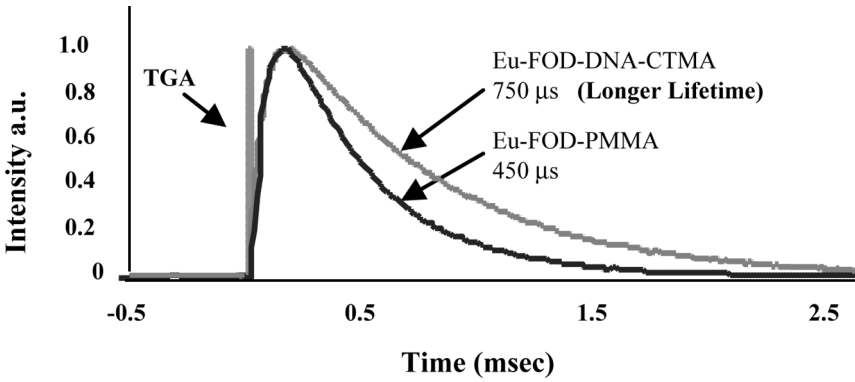


FIGURE 17 Relaxation of emission from Eu-FOD-DNA-CTMA and Eu-FOD-PMMA films.

CONCLUSIONS

We have presented several examples of marine DNA based materials for use in passive and active photonic applications. DNA-CTMA is a promising optical waveguiding material. It has demonstrated the potential for use as both top and bottom cladding layers for NLO polymer based EO devices. It has demonstrated excellent optical and electromagnetic properties thus far, as well as excellent processability and compatibility characteristics. Our preliminary work also suggests that marine DNA could be applied to optical memory, light amplification and electro-optic systems.

We would like to note, however, that the experiments conducted thus far have not been optimized. Additional experiments and testing are necessary and planned to further characterize both DNA-CTMA and the dye:DNA-CTMA based materials. Determination of the long term stability of DNA-CTMA complex based materials is one of those crucial issues.

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