NONLINEAR OPTICAL CUBIC EFFECTS IN FUNCTIONALIZED DNA

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In this paper we investigate the third-order nonlinear optical properties of DNA-based complexes using the optical third harmonic generation (THG) and degenerate four wave mixing (DFWM) techniques at a wavelength of 1064 nm and 532 nm, respectively. We found that the third-order susceptibility ($\chi^{(3)}$) of DNA-based films in the case of THG was about one order of magnitude larger than that of our reference, a pure silica slab. In thin films doped with 5% of the chromophore Disperse Red 1 (DR1), a two order of magnitude larger value of $\chi^{(3)}$ was observed. Also, in the case of DFWM the $\chi^{(3)}$ values of the guest-host system DNA-CTMA-DR1 was one (10%) or two (15%) orders of magnitude larger than for guest or host systems alone.

1. Introduction

Nucleic acids and their derivatives has attracted a lot of attention for their important biological role [1,2]. Due to physical optical and electromagnetic properties DNA is a subject of interest for potential applications in photonics and electronics [3-5]. However, DNA by itself is an optically passive material and it is necessary to functionalize it with photoresponsive molecules. These molecules can be included in the DNA matrix by intercalation in stacked layers of nucleic acid bases of the helix, by inserting into the major and minor grooves of DNA helix or by electrostatically stacking on the surface of DNA helix [6-8]. The DNA molecule can also be characterized by several types of active centres. These include the oxygen ions of the phosphate groups, which bear the negative charges, some of the N bases (N_7 guanine and adenine, N_3 cytosine) and the oxygen atoms of guanine, thymine and cytosine.

DNA-based materials, or inorganic salts of DNA, are water-sensitive and have insufficient mechanical strength for the fabrication of optical and optoelectronic devices. Also, the double helix is suppressed at temperatures above 90°C, making direct application to photonic and electronic devices improbable. Significant progress in the temperature stability was made by the Chitose Institute of Science and Technology (CIST) group [9], demonstrating that complexes of DNA and a hexadecyltrimethylammonium-chloride (CTMA) surfactant are stable up to 230°C. They are also water insoluble, but soluble in a number of alcohol solvents. These complexes have been processed into good optical waveguide quality thin films by the spin deposition [10,11].

In this paper we report some results obtained in the fabrication of DNA-CTMA thin films, as well as thin films doped with an active NLO molecule, Disperse Red 1 (DR1) chromophore. The films were characterized by UV and visible spectroscopy and their third-order NLO response was measured by the optical third harmonic generation technique.

Also, the system guest-host (DNA-CTMA-DR1) were studied using degenerate four wave mixing technique. This method give us more information about third order nonlinear susceptibility than THG.

2. Experimental

2.1. Preparation of DNA-surfactant complexes and doped solution and thin films

DNA sodium salts, extracted from salmon milt and roe was provided by CIST. The molecular weight measured $M_W = 10^6$ Daltons (Da) or 2000 base pairs. The chromophore, 4-(4-Nitrophenylazo)diphenylamine (DR1), purchased from Aldrich, was purified by a double recrystallization from an absolute methanol solution. The CTMA surfactant and solvents used were also purchased from Aldrich and used as supplied, without any further purification.

The DNA was separated from other constituents, present in salmon milt and roe. The high molecular weight DNA rendered inhomogeneous film thickness due to high solution viscosity. In order to reduce the viscosity of the DNA-based solutions an ultrasonic procedure was used [11].

After sonication, a 6 g/L concentration of DNA in 18 MΩ cm deionized water, at 20°C, was blended using a magnetic stirrer overnight. The CTMA, with a slightly higher concentration (6.2 g/L), was dissolved under the same conditions in 18 MΩ cm deionized water, at 20°C, overnight. One liter of the aqueous DNA-Na$^+$ solution was then added drop-wise to one liter of aqueous CTMA solution and stirred at room temperature for 6 hours. The DNA-CTMA precipitate complex was collected by vacuum filtration through a 0.4 μm nylon filter, washed with 18 MΩ cm deionized water and then dried in a vacuum at 35°C.

The DNA–CTMA complex was dissolved in butanol and was also functionalized with DR1. The concentration of DR1 to DNA-CTMA was 5, 10, 15 wt%. The resulting solutions of DNA-CTMA and DNA-CTMA-DR1 complexes were then filtered through a 0.2 μm pore size nylon syringe filter.

The glass substrates used were carefully cleaned in a commercial surfactant using ultrasonication and washed several times in deionized water. The cleaning procedure was ended by baking in a 200°C oven for 60 minutes.

Spin deposition was used to fabricate thin films of both DNA-CTMA and DNA-CTMA-DR1 with controlled thickness on BK7 glass slides. The principle of deposition (of the mixture with certain viscosity) is based on a homogeneous spreading out of the solution on the rotating substrate with an angular speed of 1000-1500 rpm. Immediately after the deposition, the thin films were cured in an 80°C oven for 60 minutes in order to eliminate any remaining solvent.

In DFWM experiment, in which DNA-CTMA-DR1 was studied in solution, the measured third order nonlinear optical susceptibility can be considered as the combination of the responses of the solute and the solvent. We used butanol as solvent for DNACTMA-DR1 guest-host system (Concentration: C_{DR1}=0.8 g/L).

The strong UV absorption band at around 260 nm is clearly seen in the first two absorption spectra (cf Fig. 1, spectra 1 and 2). This absorption band corresponds to the $\pi-\pi^*$ transition of electrons of C=C bond of DNA bases. The absorption band at around 480 nm in DNA-CTMA-DR1 (cf Fig. 1., spectrum 2) is similar to that of pure DR1 (cf Fig. 1, spectrum 3), showing minor solvent influence (solvatochromic effect). This maximum absorption for DR1 is also observed for the thin film case in Fig. 2.
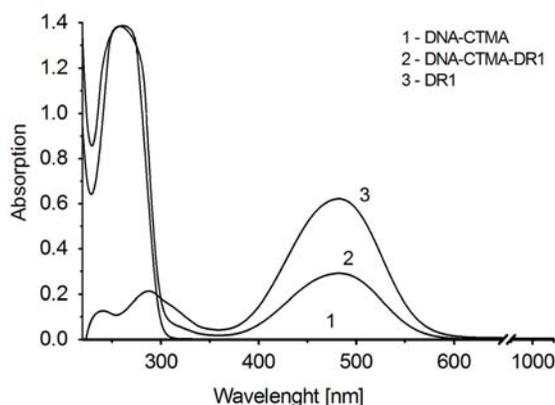

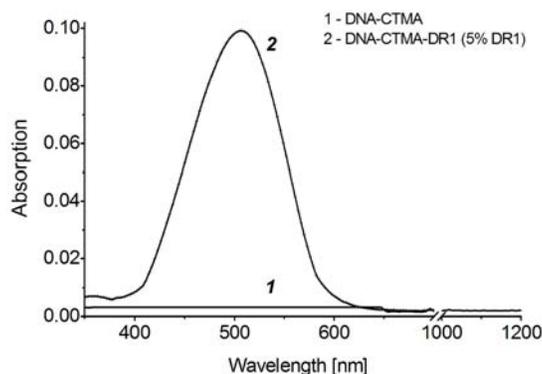*Fig. 1. Absorption spectra of: 1-DNA-CTMA, 2-DR1-DNA-CTMA (5% DR1)*
and 3 - DR1 solutions.

Fig. 2. Absorption spectra of: 1 - DNA-CTMA and 2 - DR1-DNA-CTMA (5% DR1) thin films.

2.3. Third harmonic generation

The THG response of thin film was measured with a Q switched Nd:YAG laser with 13 ns pulse duration at 1064 nm and 10 Hz repetition rate. In THG method (Fig. 3), the sample deposited on BK7 glass substrate were mounted on a rotation stage (kept in vacuum in order to avoid air contribution) and Maker fringes were generated by rotating the sample around the axis perpendicular to the beam propagation direction and coinciding with it. The quarter wave plate ($\lambda/4$) transforms the linearly polarized light into circularly polarized light and the polarizer P then selects the incident beam polarization. Since the measured samples were isotropic, s polarization was used.
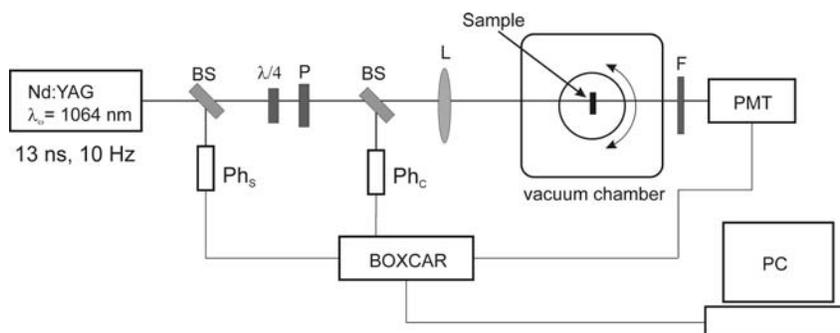

Fig. 3. Schematic representation of THG experimental setup. BS – beam splitter, $\lambda/4$ – quarter wave plate, P – polarizer, L – convergent lens (25 cm), F – filters (with selective filter: 355 nm), Ph_S, Ph_C – synchronization and control photodiodes, PMT – photomultiplier tube.

The THG intensities were calibrated with THG measurements on a high purity silica slab, performed under the same conditions. Typical plots of THG intensities versus incidence angle are presented in Fig. 4 (from the glass plate alone (a), the glass plate with the DNA-CTMA film (b) and the glass plate with the DNA-CTMA-DR1 thin film). Figure 4 presents also the theoretical fitting results of THG signal (solid lines). For the glass slide alone, the Maker fringes, due to the interference of the free and bound waves in the glass slab, can be seen. This is due to the fact that the glass slab thickness (1040 μm) is much larger than the coherence length (7.4 μm). In Figs. 4b and 4c, a monotonically, incident angle dependent, THG contribution from thin films of DNA-CTMA and DNA-CTMA-DR1 is clearly observed. These contributions are decreasing with the incidence length due to the fact that the film thickness is comparable to the coherence length. The decrease is governed by the envelope function (increasing reflection of fundamental and harmonic beams with increasing incidence

angle). It is also seen that in the case of the DR1 doped film (Fig. 4c) the contribution is much more prominent than for the undoped film (Fig. 4b).

In order to get precise value for the thin films susceptibility $\chi^{(3)}$ the THG intensities were fitted with the formulas derived by Kajzar, *et. al.*, [13]. The results of the fit are shown by the solid lines in Fig. 4. A good agreement is observed between the calculated and measured THG intensities. For the fitting procedure, the values of the refractive index for DNA-CTMA that were reported by Grote, *et. al.*, [14] were used. For DNA-CTMA-DR1 the same refractive indices were used as for DNA-CTMA. Indeed, for the relatively small concentration of DR1, we do not expect a significant change of the refractive index in the doped film. Also, in the case of THG in thin films, the harmonic intensities do not depend on the difference of refractive indices. A correction for the absorption at the harmonic wavelength in the DNA-CTMA-DR1 film was applied by introducing a complex index of refraction in the calculations. For silica and glass slab the tabulated values for the refractive indices were used and the slab thickness was determined from the fit. Independent THG measurements on a clean glass slab were also performed to calibrate the data with the THG measurements on a silica slab.
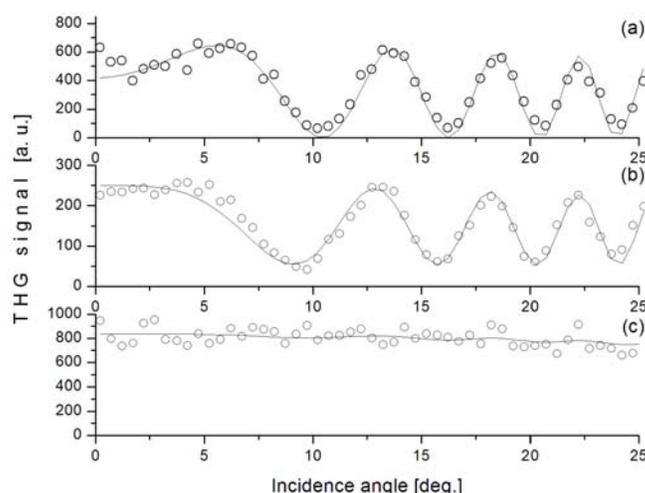

Fig. 4. THG intensities for the: (a) - glass substrate, (b) - glass substrate + DNA-CTMA thin film and (c) - and glass substrate + DNA-CTMA-DR1 thin film as a function of the incidence angle.

2.4. Degenerate four wave mixing

The DFWM response of solution was measured with a mode-locked Nd:YAG laser with 30 ps pulse duration, the repetition rate of 1 Hz and 532 nm wavelength. The intensity at the input face of the sample is taken to be Gaussian distribution in space and time. In DFWM measurement (Fig. 5), two pump beams were counter-propagating with the remaining 6% going to the probe beam. The probe beam was a small nonzero angle (θ=12°) with respect to the pump beams. The three beams of the same frequency (ω) were temporally and spatially overlapped in the sample. A phase-conjugated signal generated from the three laser beams was collected at a reverse direction of the probe beam. The $\chi^{(3)}$ measurements were carried out with polarization directions of all three interacted laser beams aligned vertically (*xxx*). The incident wave intensities verify the relations: $I_1(z=0)=I_2(z=L)$ and $I_3=6\times10^{-2}I_1$ (it means that 94% of the laser power was evenly split between the two counter-propagating pumps pulse with the remaining 6% going to the probe pulse). The phase-conjugated signal was detected by a photo-multiplier tube (PMT). A portion of the input beam was picked off and measured by a photodiode (Ph$_c$) to monitor the input energy. CS$_2$ was used as a reference material. The third order nonlinear susceptibility of CS$_2$ is estimated to be $\chi^{(3)}$=6.5×10^{-13} esu.
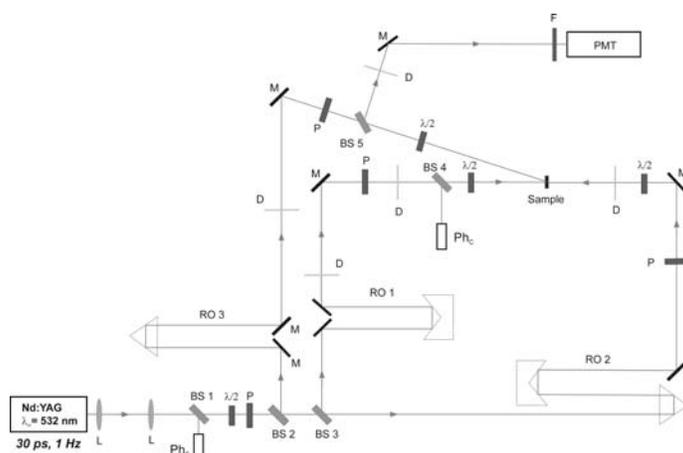
Fig. 5. Degenerate four wave mixing experimental setup: L – lens, M – mirrors, D – diaphragms, λ/2 – half wave plates, RO - delay lines, P - glan prism, Phs, Phc – synchronization and control photodiodes, F – filters, BS - beam splitters, PMT - photomultiplier tube.

3. Results and discussion

The values derived from measurements for THG susceptibilities of the materials investigated in this study are listed in Table 1. For the silica calibration we used the value determined recently by Gubler and Bosshard [15] ($\chi^{(3)}$=1.43±0.14), which is about two times smaller than previously reported [16]. In the case of DNA-CTMA films we observe the value of THG susceptibility about one order of magnitude larger than for silica. This difference may be well accounted for by the presence of highly polarizable conjugated π electrons in DNA. For the doped DNA-CTMA complex with only 5% of DR1, we observed THG susceptibility two orders of magnitude larger than for fused silica. This increase is due to nonlinear response of the doping chromophore DR1 (we expect two photon resonance for the 532 nm wavelength). Indeed, the double of the fundamental photon energy 2ω matches with the transition energy to the first excited singlet state. For the DNA-CTMA the response is coming from DNA, as CTMA molecules do not contain conjugated π electrons, known to be at the origin of large nonlinear response in organic.

Table 1. Third order NLO susceptibilities $\chi^{(3)}$.

Compound	Thickness[μm]	Refractive Index n_ω	Coherence Length [μm]	$\chi^{(3)} \times 10^{-14}$ [esu]
DNA-CTMA	0.367	1.488 [14]	7.4 [14]	11.5±0.12
DNA-CTMA-DR1 (5%)	3.484	1.488	7.4	155±16
DNA-CTMA-DR1 (10%)	4.060	1.488	7.4	69±7
DNA-CTMA-DR1 (15%)	3.484	1.488	7.4	85±9
glass plate	1041	1.50664	5.62	2.11±0.2
silica	1010	1.44967	6.71	1.43±0.14 [15]

Nonlinear optical properties on solutions of guest-host system were investigated using degenerate four wave mixing (DFWM) method. The values of linear absorption coefficient (α), two photon coefficient (β) and third order nonlinear optical susceptibility ($\chi^{(3)}$) were calculated using model described by Sahraoui and Rivoire [17] and are collected in table 3.
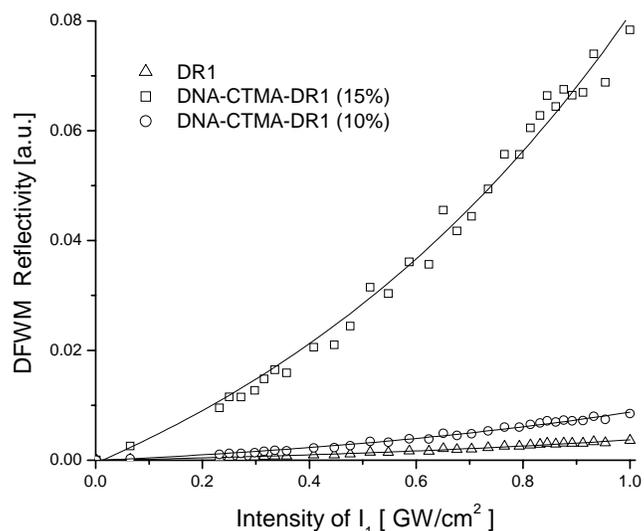
Fig. 6. The DFWM reflectivity of DR1 and DNA-CTMA-DR1 (with 10% and 15% of DR1) as a function of incident pump intensity.

Table 3. The values of the linear absorption coefficient (a) and the absolute values of the third order nonlinear optical susceptibility ($\chi^{(3)}$) of DR1, DNA-CTMA and guest-host system (DNA-CTMA-DR1) dissolved in butanol (DR1=0.8 g/L - 10%, 12 g/L - 15%).

Samples	α [cm^{-1}]	β [cm/GW]	$Im\ \chi^{(3)}\ \times\ 10^{-12}$ [esu]	$\chi^{(3)}_{DFWM}\ \times\ 10^{-12}$ [esu]
DNA-CTMA in butanol	0.3	≈ 0	-	0.706
DR1 in butanol	88.05	1.49	63.9	6.90
DNA-CTMA-DR1 10%	64.38	≈ 0	-	16.3
DNA-CTMA-DR1 15%	76.01	≈ 0	-	151

From obtained results is seen that the third order nonlinear optical susceptibilities ($\chi^{(3)}$) of host-guest system DNA-CTMA-DR1 increase with comparison with the value of the third order nonlinear optical susceptibilities of dyes. We supposed that this is caused by increase of the charge transfer effects and of the dipole moments of the molecule with the increase of the chain length.

4. Conclusions

The nonlinear optical properties of DNA-CTMA-DR1 thin films were characterized using the third harmonic generation. This method gives the fast electronic part of cubic susceptibility. We observe an almost one order of magnitude larger value of $\chi^{(3)}$ for pure DNA-CTMA thin film than for the reference material (fused silica). This increase is apparently due to the presence of conjugated π electrons in nucleobases. In doped films with DR1 the largest increase, by an order of magnitude with respect to the pure host and by two orders of magnitude with respect to silica is observed in thin films of DNA-CTMA doped with 5% of DR1. For higher concentration we observe a much lover increase, not following the chromophore concentration. This my be

accounted for by a possible two photon resonance contributions to $\chi^{(3)}$ susceptibility in DR1 containing films. This suggests DNA might prove an interesting alternative for photonics applications. The DNA complexes with surfactants, such as CTMA, are very stable. They are ecologically friendly, as DNA is recovered from waste from the fishing industry and is biodegradable. The DNA-CTMA complex can be doped with active NLO molecules.

The guest-host system of DNA-CTMA-DR1 were measured by using DFWM technique. The significant enhancement of $\chi^{(3)}$ that we have observed using DFWM experiment show clearly that this system could be a new potential class of materials for nonlinear optical devices.

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