

# Nonlinear optical characterization of DNA based azo-polymers

H. EL OUAZZANI<sup>1\*</sup>, O. KRUPKA<sup>2</sup>, V. SMOKAL<sup>2</sup> AND B. SAHRAOUI<sup>1</sup>

<sup>1</sup>Moltech Anjou Laboratory, CNRS UMR 6200, University of Angers, 2 Bd Lavoisier, 49045 Angers

<sup>2</sup>Taras Shevchenko National University of Kyiv, 60 Volodymyrska, 01033 Kyiv Ukraine

Received: October 20, 2015. Accepted: November 3, 2015.

The nonlinear optical response of spin deposited thin films of DNaCTMA-azobenzenes has been investigated by means of THG Maker fringes measurements at a fundamental wavelength of 1064 nm. In that case, the measurements were performed using an Nd:YAG laser as the excitation source with 30 ps laser pulses. A theoretical and experimental study is presented for of conjugated systems associated to the DNA. A strong enhancement of the THG signal is observed which is related to the different charge transfer within the molecules.

*Keywords: DNA based azo-polymers, conjugated systems, NLO, THG*

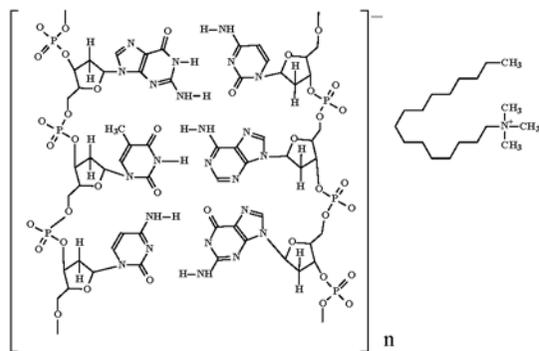
## 1. INTRODUCTION

DNA plays a crucial role in all living organisms because it is the molecule which carries the genetic code. For this reason, one of the important goals of biophysics branch is to understanding of the physical properties of the DNA molecule, one of the most important molecules for life. Actually, experimental studies have provides a wealth of information about DNA. Coupling these experimental results with theoretical considerations has led to substantial progress in deciphering the secrets of DNA [1].

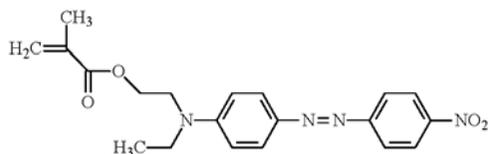
This work has dealt with the different structural conformations of the couple DNA azopolymers systems and the NLO response while passing from a conformation to another. So, we report the study of optical third harmonic generation (THG) on this systems and the the magnitude of third-order nonlinear susceptibility  $\chi^3$ . These measurements were performed by the standard

---

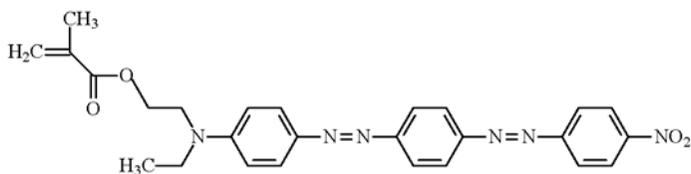
\*Corresponding author e-mail: hasnaa141@hotmail.com



DNACTMA



S1



S2

FIGURE 1

The chemical structure of DNACTMA surfactant complex; S1 and S2.

Maker fringe method [2], with a  $\text{SiO}_2$  reference sample [3-5], and were produced on the samples in the transmission direction by varying the incident angle. Specially, a comparative study is made between the new systems (Figure 1) is presented with a respect to the impact of the electron-acceptor group and the charge transfer within the azobenzene moieties.

## 2. MATERIALS

NLO dyes with large conjugated  $\pi$ -systems and dipole moments are effective for inducing a large NLO response, and the push-pull substi-

tuted azobenzene dye Disperse Red 1 (DR1) has been investigated widely in this field [6-8]. The push-pull organic chromophores are molecules consisting of electron donor (D) and electron acceptor (A) moieties typically bridged together by a  $\pi$ -conjugated organic backbone. Another characteristic of these materials is the variation of certain molecular properties with the effective size of the conjugate system. The idea is to connect these nonlinear systems to the molecule of DNA to study the effect of adding this bio-molecule on the enhancement of the nonlinear optical response.

The DNA used in our study was provided by Chitose Institute of Technology (CIST), Japan. DNA sodium salt ( $M_w$ :  $1.3 \times 10^6$ , ca. 2000 base pairs). It was extracted from salmon milt and roe. In order to decrease the viscosity of DNA solutions the ultrasonic procedure was used [9]. After sonication, a 6 g/L concentration of DNA in 18 M $\Omega$  cm deionized water, at 20°C, was blended using overnight a magnetic stirrer. The CTMA, with a slightly higher concentration (6.2 g/L), was dissolved under the same conditions in 18 M $\Omega$  cm deionized water, at 20°C, overnight. One liter of the aqueous DNA-Na<sup>+</sup> solution was then added drop-wise to one liter of aqueous CTMA solution and stirred at room temperature for 6 h. The DNaCTMA precipitate complex was collected by vacuum filtration through a 0.4  $\mu$ m nylon filter, washed with 18 M $\Omega$  cm deionized water and then dried in vacuum at 35°C. As already mentioned the complex is soluble in common organic solvents but insoluble in water. In the next stage, the DNaCTMA complex (C = 80 g/L) was dissolved in butanol and functionalized with azo derivatives (C = 1.2 g/L). The solutions of azo derivatives-DNaCTMA complex were filtered through a 0.4  $\mu$ m nylon filter before using.

4-((2-Methacryloyloxyethyl)ethylamino)-4-nitroazobenzene (S1). Azomonomer was synthesized in the same way as reported [10]. The solid was recrystallized from methanol. Dark red crystals m.p. 83 °C, yield 80%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.35 (d, 2H, Ar), 7.92 (t, 4H, Ar), 6.85 (d, 2H, Ar), 6.1 (s, 1H, CH<sub>2</sub>), 5.6 (s, 1H, CH<sub>2</sub>), 4.38 (m, 2H, OCH<sub>2</sub>), 3.75 (m, 2H, NCH<sub>2</sub>), 3.56 (m, 2H, NCH<sub>2</sub>), 1.94 (s, 3H, CH<sub>3</sub>), 1.24 (m, 3H, CH<sub>3</sub>). UV-VIS (THF):  $\lambda = 475$  nm.

4-((2-Methacryloyloxyethyl)ethylamino)-4'-(4-nitrophenylazo)azobenzene (S2). Azomonomer M3 was synthesized in the same way as azomonomer S1. Dark purple crystals; yield 60 %; mp 160 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.40 (d, 2H, Ar), 8.12-7.92 (m, 8H, Ar), 6.85 (d, 2H, Ar), 6.12 (s, 1H, CH<sub>2</sub>), 5.61 (s, 1H, CH<sub>2</sub>), 4.38 (t, 2H, OCH<sub>2</sub>), 3.75 (t, 2H, NCH<sub>2</sub>), 3.55 (q, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 1.97 (s, 3H, CH<sub>3</sub>), 1.28 (s, 3H, CH<sub>3</sub>). UV-VIS (THF):  $\lambda = 340, 502$  nm.

The study was made for these systems in the form of thin layers. The preparation procedure is described in the following.

### 3. THIN FILMS PROCESSING

Thin films of azobenzenes-DNACTMA complex were obtained by spin coating of filtered solutions through a 0.4  $\mu\text{m}$  pore size nylon syringe filter 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 800 rpm. We used as solvent 1,1,2-trichloroethane for the quality of thin film formation. The same polymer concentration of 56 g/l was used. Immediately after the deposition, the films were cured in an oven at 50°C and for 180 minutes in order to eliminate any remaining solvent.

Then, the thickness of the samples was measured using a profilometer and was found about 1.1  $\mu\text{m}$  for S1 and 1.7  $\mu\text{m}$  for the S2.

### 4. EXPERIMENTS

The third-order nonlinear optical properties of spin deposited thin films was investigated using the optical THG technique. It consists in detecting the intensity of the generated beam at third-harmonic frequency as a function of the incidence angle of the fundamental beam.

The advantage of the THG technique is that it can provide information only about the electronic contribution to the  $\chi^{(3)}$  without being influenced from generally slower contributions like molecular orientation. Even, THG is possible for the systems with a center of inversion unlike the second harmonic generation process (SHG) [11].

In that case, the measurements were performed on thin films using an Nd:YAG laser as the excitation source. It provides 30 ps pulses duration at 1064 nm wavelength, with a frequency of 10 Hz.

For THG Maker-fringe, the signal was recorded on a rotating sample for incidence angles. For these experiment a half-wave plate has been seated after a polarizer in order to set the incident polarization either parallel (p) or perpendicular (s) to the incidence plane. An analyzer was positioned after the sample, allowing measurements on different polarizations configurations. To increase THG efficiency, the laser was focused onto the DNA samples by a lens of 25 cm focal length. The films deposited on transparent substrates, were mounted on a rotation stage in order to perform angle dependent THG-measurements. After, the beam passes through a KG3 filter, which cut out the fundamental beam and an interferential optical filters (at 355 nm) to preserve only the THG signal. Also the density filters were used in order to reduce the intensity involved from the nonlinear medium.

Third harmonic signal was detected by photomultiplier tube (Model: Hamamatsu), and the output of the PMT was amplified and averaged by a boxer integrator.

Finally, Maker fringes were obtained, which were generated by rotating the sample. The THG-device was calibrated using a fused silica ( $\text{SiO}_2$ ) which is frequently used as a reference material for cubic NLO-effects because its

optical constants are well known. Its third order nonlinear optical susceptibility was estimated to be  $\chi^3 = 2.0 \times 10^{-22} \text{m}^2 \text{V}^{-2}$  [12].

## 5. RESULTS AND DISCUSSIONS

Figure 2 illustrate the thin film absorption spectra of DNaCTMA, S1-DNaCTMA and S2-DNaCTMA respectively. A strong UV absorption band is seen in Fig. 2 for all systems, with the maximum absorption wavelength about 260 nm, corresponding to the  $\pi-\pi^*$  transition of electrons of the C=C bond of the DNA bases. In the case of azobenzene doped films, another absorption band which considered as a charge transfer band between the electron donor and electron acceptor groups.

Then, comparative Maker fringes measurements were done for the systems S1 and S2 using different excitation-detection polarization configurations ss, ps and pp. Figure 3 shows the results obtained for the S1.

There is significant difference of the obtained THG magnitude between the three configurations of polarization studied as expected. Similar behavior has been found for the system S2 as shown in the figure 4.

For the analysis of the THG measurements and because the third harmonic signal is in a spectral position, where the linear absorption of the samples is important, the following equation has been used [13-14]:

$$T = \left( \frac{I_{fs}}{I_s} \right) (1 - R_s)$$

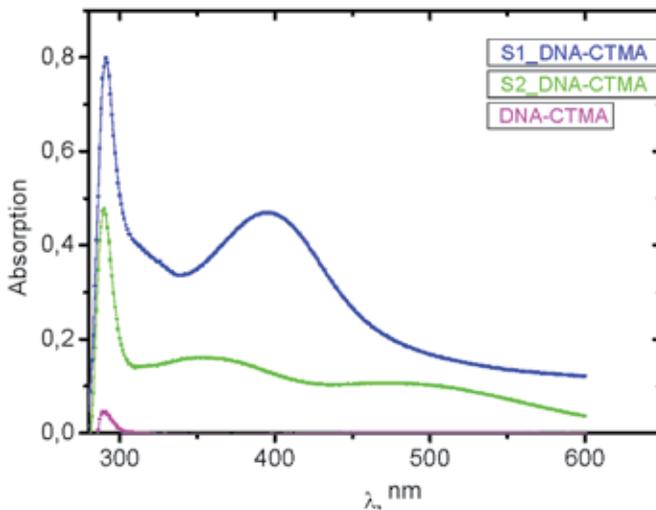


FIGURE 2  
Absorption spectra for the studied systems.

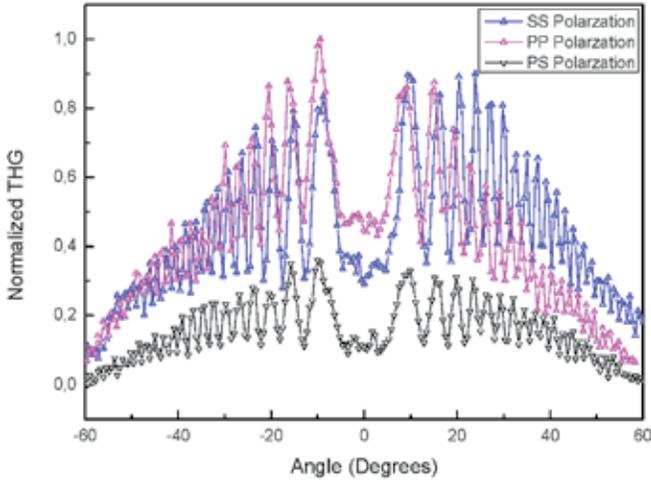


FIGURE 3

Third harmonic generation maker fringes for the system S1 deposited on glass substrate.

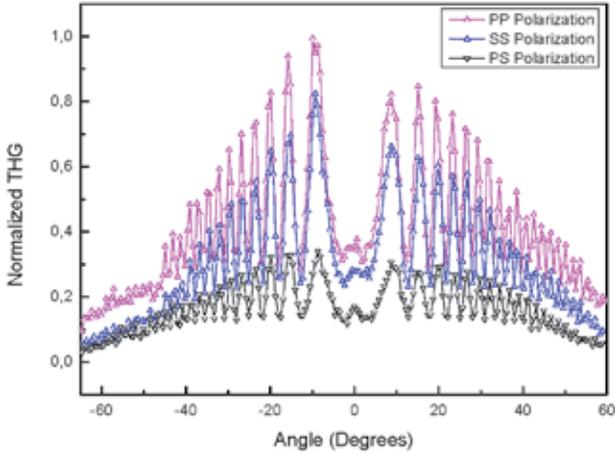


FIGURE 4

Third harmonic generation maker fringes for the system S2.

Where  $\chi^{(3)}$  and  $x_s^{(3)}$  are the third-order nonlinear susceptibilities of the sample and the reference material, respectively,  $I_c$  is the coherence length of fused silica,  $I$  is the film thickness,  $\alpha$  is the linear absorption coefficient at the fundamental wavelength, and  $I^{3\omega}$  and  $I_s^{3\omega}$  are the peak intensities of the Maker fringes pattern of the film and the fused silica slab, respectively.

TABLE 1

The third order nonlinear optical susceptibility results, for azobenzenes-DNACTMA systems, determined by THG technique.

Samples	$c^{(3)} (10^{-22} \text{ m}^2/\text{V}^2)$		
	SS	PP	PS
S1-DNACTMA	32,2	32,8	19,3
S2-DNACTMA	53,7	58,6	32,8

In general, this model compares the maximum amplitudes of light intensities of the third harmonic of the medium studied with those of the reference material that is a fused silica  $\text{SiO}_2$  at 1064 nm [12]. It is valid in the case where the thickness of the film is much lower than the coherence length and also that the signal coming from the substrate can be considered to be negligible compared to the signal emanating from the film which was the case in our investigation. The signal from the substrate was measured separately and its contribution has been removed from the signal obtained from the thin film sample.

Then, the nonlinear susceptibility of the third order  $c^{(3)} \chi^{(3)}$  was calculated for every sample and in different conformation of the polarization (pp, ss and ps) the aim of which of conformation represents a significant non-linearity, which means, conformation where a maximum degree of signal is observed. Table 1 present the values found in the three conformations.

In Table 1, the values of non-linear susceptibility of the third order are illustrated. Strong non-linearity is observed for the systems S2 compared to S1. Also, the PP configuration has resulted in the highest nonlinear optical response. Intermediate efficiency has been obtained for the SS configuration, while the PS corresponded to the lowest THG efficiency.

This enhancement of the charge-transfer efficiency can be attributed to the additional phenyldiazene fragment in the side chain S2. The compounds with strong hyperpolarizability must have in their ends substituent with donor or acceptor character as strong as possible [15-16]. Generally, the existence of the conjugate allows the spread of electronic influences along the squellette, especially the deformability of the  $\pi$ -electron cloud is easy which leads to a large polarizability.

In all cases, the results obtained for these new systems are promising and the values were found higher than the reference material.

## 6. CONCLUSION

We have synthesized and measured the third-order optical nonlinearity of thin films of azobenzenes-DNACTMA systems by the Maker fringes techniques. We have shown that these systems have very high nonlinearities of

third order due to the conjugation and the fragments of donor-electron acceptor group. This therefore results in a change of charge transfer in the molecule as well as the high impact on the NLO response. The significant nonlinear optical response combined with the possibility to further modify it, by changing the conjugation, the electron acceptor and the electron donor groups, suggests that these systems can prove to be important candidates in biophotonics.

## REFERENCES

- [1] A. Szabo, Y. Wang, S. A. Lee, H. J. Simon, and A. Rupprecht, *Biophysical Journal* **Volume 65** December 1993.
- [2] F. Kajzar, J. Messier, C. Rosilio, *J. Appl. Phys.* **60** (1986) 3040.
- [3] R.C. Miller, *Appl. Phys. Lett.* **5** (1964) 17.
- [4] C.G.B. Garrett, F.N.H. Robinson, *IEEE J. Quantum Electron.* **2** (1966) 328.
- [5] B. Buchalter, G.R. Meredith, *Appl. Opt.* **21** (1982) 3221.
- [6] Nahata, A.; Shan, J.; Yardley, J. T.; Wu, C. *J. Opt. Soc. Am. B* 1993, **10**, 1553.
- [7] Singer, K. D.; Kuzyk, M. G.; Sohn, J. E. *J. Opt. Soc. Am. B* 1987, **4**, 968.
- [8] Singer, K. D.; Sohn, J. E.; Lalama, S. J. *Appl. Phys. Lett.* 1986, **49**, 248.
- [9] E. Heckman, J. Hagen, P. Yaney, J. Grote, F. Hopkins, *Appl. Phys. Lett.* **87** (2005) 211115.
- [10] Singer, K. D.; Kuzyk, M. G.; Sohn, J. E. *J. Opt. Soc. Am. B* 1987, **4**, 968
- [11] H. El Ouazzani, K. Iliopoulos, M. Pranaitis, O. Krupka, V. Smokal, A. Kolendo, and B. Sahraoui, [dx.doi.org/10.1021/jp109936t](https://doi.org/10.1021/jp109936t), 2011, 115, 1944–1949.
- [12] Gubler, U.; Bosshard, C. *Phys. Rev. B* 2000, **61**, 10702.
- [13] Sahraoui, B.; Luc, J.; Meghea, A.; Czaplicki, R.; Fillaut, J.-L.; Migalska-Zalas, A. *J. Opt. A: Pure Appl. Opt.* 2009, **11**, 1.
- [14] Kanbara, H.; Maruno, T.; Yamashita, A.; Matsumoto, S.; Hayashi, T.; Konami, H.; Tanaka, N. *J. Appl. Phys.* 1996, **80**, 3674.
- [15] S. R. Marder, D. N. Beratan et L.–T. Cheng, “Approches for optimizing the first electronic hyperpolarizability of conjugated organic molecules”, *Science* 252, pp. 103–106 (1991).
- [16] S. R. Marder, J. W. Perry, G. Bourhill, C. B. Gorman, B. G. Tiemann et K. Mansour, *Science* **261**, pp. 186–189 (1993).