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DNA – novel nanomaterial for applications in photonics and in electronics

ADN – nanomatériau nouveau pour les applications en photonique et en électronique

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Cellule électrochromique solide

ABSTRACT

Functionalization with surfactants and with active molecules of deoxyribonucleic acid (DNA), thin film processing as well as their nonlinear optical and electrical properties are reviewed and discussed. On the basis of a quantum three level model, we show that the anomalous concentration variation of cubic susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ in thin films of DNA–CTMA complexes doped with Disperse Red 1 chromophore can be explained by the concentration variation of two-photon resonance contribution. We show also that the DNA complexes, plasticized with glycerol and adequately doped can be processed into self standing conducting membranes with a high electrical conductivity. The measured ionic conductivity at room temperature, depending on dopant used and its concentration, is in the range of 3.5×10^{-4}–10^{-5} S/cm and increases linearly as a function of temperature, reaching 10^{-3} S/cm at 358 K for the most conducting sample, obeying predominantly the Arrhenius law. Practical applications of DNA complexes are also described and discussed.

RÉSUMÉ

Fonctionnalisation de l'acide désoxyribonucléique (ADN) avec des composées tensioactifs et avec les molécules actives, la fabrication des films minces ainsi que leurs propriétés optiques linéaires, non linéaires et électriques sont examinées et discutées. Avec l'aide d'un modèle quantique à trois niveaux nous montrons que la variation anormale de la susceptibilité cubique en fonction de la concentration du chromophore dans des films minces faits à partir des complexes ADN–CTMA, dopés avec le Disperse Red 1, peut être expliquée par le déplacement de la bande d'absorption. Nous décrivons également comment l'ADN peut être plastifié et transformé en membranes conductrices. La conductivité électrique de ces membranes peut être contrôlée par un dopage adéquat avec des ions ou polymères conducteurs. Les membranes obtenues montrent une conductivité électrique élevée. La conductivité, mesurée à l'ambiante, varies entre de 3.5×10^{-4} et 10^{-5} S/cm en fonction du dopant utilisé. Elle croit avec la température, pour attendre ca 10^{-3} S/cm, dans le meilleur cas, à 358 K, en obéissant essentiellement la loi d'Arrhénius. Les applications pratiques des complexes dérivés de l'ADN sont également décrites et discutés.

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1. Introduction

Since the discovery of its structure by Watson and Crick [1,2] in 1953, deoxyribonucleic acid (DNA) attracted much interest from biologists, chemists, and later, from physicists. Indeed, this supramolecule exhibits a peculiar double helix structure, consisting of base pairs of molecules: adenine with thymine and guanine with cytosine, and of helix backbones made of sugar and phosphate groups, joined internally by the ester bonds. The base pairs are linked together by the strong hydrogen bonds. Because the outside groups are phosphates, the DNA macromolecule presents a net negative charge, compensated by sodium ions, nonlocalized counter ions, which can move freely along the macromolecular chain surface [3].

DNA biopolymer plays essential role in the growth, development and heritage transmission of living species of not only humans and animals but also of the vegetal ones. The encoding of genetic information of given species is contained in the sequence of base pairs.

The size of DNA depends on the level of development of the given species. Usually it is expressed in the number of base pairs (bp) and spans from several tens of bp, as for *Escherichia coli* (76 bp), to 3000 Mbp for human DNA [4]. There are many programs on the Internet which transform the base pairs number into molecular mass (daltons). The diameter of the helix is about 2 nm and the distance between the two base pairs is ca. 3.4 nm.

One of the important arguments developed in favor of biopolymers for replacing the synthetic polymers in photonics and in electronics, and particularly by DNA, is its abundance and renewability. DNA is usually obtained from the waste produced by food processing industry. Thus it can be cheap. On the contrary to synthetic polymers, if not protected, biopolymers are biodegradable. Thus their use should permit the decrease in pollution due to slowly decomposing synthetic polymers. This is comforted by the present scientific policy related to the humanity problem of creation of a sustainable society with durable development, disposing renewable resources and minimizing the environment pollution.

Besides the above mentioned advantages, there are other important properties of DNA, which are in favor of their use in photonics and in electronic, as will be shown and discussed in this article. It concerns, in particular the versatility, thin film processability and the possibility of tailoring optical and electrical properties by DNA functionalization. Its specific double strand helical structure, with minor and major groves, provides a large free volume for doping molecules as well as a good protection against photo thermal degradation. Indeed, recent photothermal degradation studies performed on a series of DNA based complexes show significantly larger first order decay constants for several chromophores embedded in than when these molecules are dissolved with the commonly used synthetic polymer the polymethyl methacrylate (PMMA). Also, DNA exhibits a higher optical damage threshold [5,6].

The article is organized as follows. In Section 2 we describe chemical functionalization of DNA. Section 3 is devoted to linear and nonlinear optical properties of functionalized polymers and in Section 4 we describe electrical properties. Practical applications are reviewed and discussed in Section 5.

2. DNA functionalization

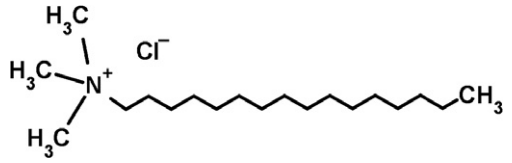
Pure DNA has a limited potential for applications in photonics. This biopolymer is soluble in water only, a solvent which does not belong to the preferred ones in device fabrication technologies, although some electronic devices containing water have been already described [7,8]. Also a week π electron conjugation, only in phenyl rings, provides limited hyperpolarizabilities to this compound. Therefore, the only possible practical use of this biopolymer in photonics is as an optically inactive material, except if its chirality can be exploited in some way.

As already mentioned, DNA offers a large free volume for functionalization as well as its ionic character. Thus its functionalization can be done by:

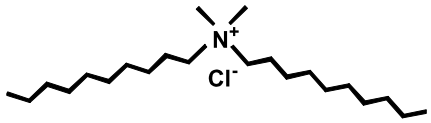
(i) electrostatic interaction;
(ii) intercalation;
(iii) statistical doping, as in the case of synthetic polymers.

DNA is known to denature at around 90 °C, changing its helical structure from double stranded to single stranded [9,10], limiting in this way the temperature range of applicability. Also thin film processing and water solubility only limit the possible range of its application.

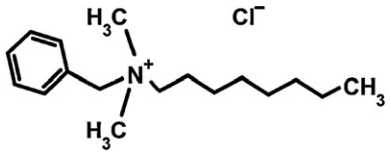
A real progress in application of DNA in photonics was made by Ogata and his collaborators, who have set up a technology for DNA extraction from the waste produced by the salmon processing industry [11–16]. They have shown that DNA reacts with the surfactant cetyltrimethylammonium chloride (CTMA) (cf. Fig. 1) forming a thermally stable, up to ca. 230 °C complex, insoluble in water, but soluble in other solvents, particularly in alcohols, such as ethanol, butanol and isopropanol. The binding force is the already mentioned electrostatic interaction between the negatively charged DNA and positively charged surfactant molecules, associated with the ion exchange. The complex is processable into good optical quality thin films [17,18] with propagation losses of 0.2 dB/cm at the telecommunication window [19]. Ogata and co-workers [11–15] have also shown that the DNA–CTMA complex shows an interesting potential for applications in optoelectronics, particularly as a matrix for active molecules, as it will be discussed later.



CTMA - cetyltrimethylammonium chloride
CTMA - chlorure de cetyltriméthylammonium



DDCA - Didecyldimethylammonium chloride
DDCA - chlorure de didécyldiméthylammonium



BA - benzalkonium chloride
BA - chlorure de benzalkonium

Fig. 1. Chemical structure of used surfactants.

Fig. 1. La structure chimique des tensio-actifs utilisés.

Recently other surfactants were found to react with DNA and form similarly stable complexes [20,21], with better solubility than DNA–CTMA (for the chemical structure of surfactants see Fig. 1), thus enlarging the spectrum of choice for doping molecules.

Thin films of DNA–CTMA complex, obtained by spin coating, were found to be partly ordered, with measured anisotropy of refractive index [22].

DNA–CTMA complexes can be doped with photosensitive molecules to provide desired electric or linear and nonlinear optical properties. This means that the DNA–surfactant complex can be used to replace the presently used synthetic polymers as host material for different kind of applications, offering several advantages such as environment protection, large free volume and a better protection of embedded in molecules. The DNA functionalization with surfactant is done in water, the only its solvent and the formed complex, insoluble in water, precipitates [11,29].

DNA–CTMA complex maintains its double stranded helical structure for temperatures exceeding 100 °C [23], which is sufficient for the majority of practical applications. It was successfully used for obtaining different functional materials. The doping is usually done in a common solvent for the complex and doping molecules, which is why the existence of a large spectrum of good solvents for the first is important for getting a large class of functional materials. In particular DNA–CTMA was doped with the well known Disperse Red 1 chromophore, commonly used for making electro-optic polymers. The polar order is realized by the active chromophore orientation with DC electric field [24]. Heckman et al. [25] have succeeded in poling thin films of DNA–CTMA–DR1 and demonstrated the first bio electro-optic modulator [26–28]. Other molecules were also successfully introduced in the DNA–CTMA matrix providing it with the desired optical or electrical properties (for a review see, e.g. Rau et al. [29]).

The DNA–CTMA complexes were also used in other kind of applications such as field effect transistor (FETs) [30], biopolymer based organic light emitting diodes (BioLEDs), as an electron blocking layer [31], or matrix for luminophores. The adequately functionalized DNA, as it will be discussed later, can be also applied in electrochromic cells for displays and for application in “smart windows” (cf. Refs. [32,33]). It is also a potentially interesting material for applications in solar energy conversion as well.

3. Linear and nonlinear optical properties

DNA and DNA–CTMA molecules exhibit a large transparency, the lowest energy absorption being that of phenyl rings, located around 270 nm. The absorption UV cut-off is around 325 nm (cf. Fig. 2), whereas in the near IR only the absorption of harmonics of high energy CH and OH vibrations are present. As shown in Fig. 3, its refractive index [34] varies between 1.582 in UV (300 nm) and 1.482 in NIR (1000 nm). It is slightly higher in UV because of the absorption of phenyl rings

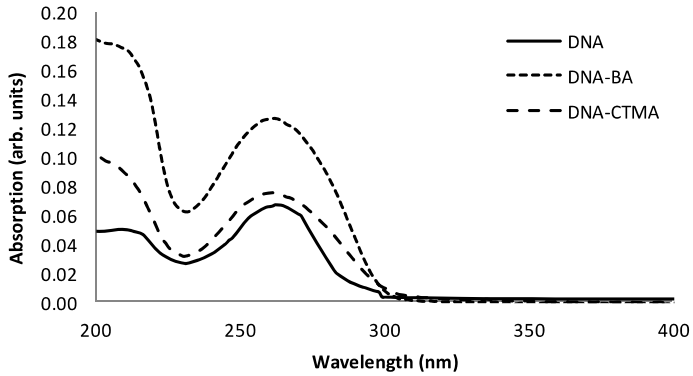


Fig. 2. Thin films optical absorption spectra of pure DNA and of two DNA–surfactant complexes.

Fig. 2. Spectres d'absorption optique films minces de l'ADN et de deux complexes l'ADN–tensioactif.

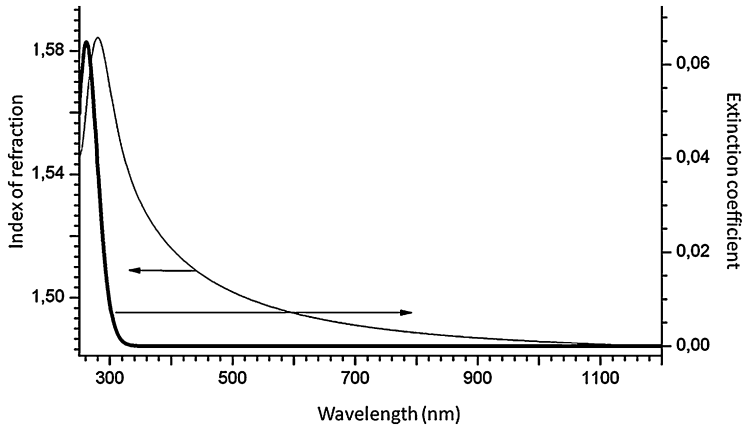


Fig. 3. Refractive index (thick line, left scale) and extinction coefficient (fine line, right scale) dispersion for a thin film of DNA–CTMA complex (after Ref. [34]).

Fig. 3. Dispersion de l'indice de réfraction (ligne épaisse, l'échelle de gauche) et du coefficient d'extinction (ligne fine, échelle de droite) pour un film mince du complexe l'ADN–CTMA (d'après Réf. [34]).

and lower in NIR than in silica. The relatively low index of refraction makes these complexes interesting for application as cladding layers in optical waveguides [35].

There is a limited number of studies of the NLO properties of pure DNA as compared to another important biopolymer, collagen (for a review see Knoesen [36] and Rau et al. [37]). Several papers were published recently, in which the second harmonic generation (SHG) is used as a tool for studying the interaction of DNA with environment or detection of its modification. In fact, SHG is a very sensitive tool to study interfaces [38], as the bulk centrosymmetry is broken there and the observation of frequency doubling is no longer forbidden by symmetry, as it is the case of centrosymmetric structures. In particular Boman et al. [39] reported on using SHG to study the formation of the DNA double helix at the quartz surface due to the pairing of adenine and thymine nucleobases. Zhuang Zheng-Fei et al. [40] used this technique as a detection tool for the very early malignancy in prostate glandular epithelial cells. Williamson et al. [41] reported observation of a humidity dependent optical SHG signal from the spun films of DNA. The SHG intensity was found to depend on the polarization of incident laser beam with respect to the helix, as it is the case of chiral structures [42].

There are also a few studies of third-order NLO properties of pure DNA. One of the first problems treated by NLO technique was the mobility of DNA helix under the applied electric field. This study is difficult for two main reasons:

(i) DNA is soluble in water only, which exhibits a large ionic conductivity. As already mentioned this solvent is also necessary to maintain its integrity;
(ii) DNA itself is a polyelectrolyte. Application of an external electric field induces an ionic dipole moment [43–45] and changes the conformation of DNA molecule [46–48].

Thus, studies have to be done carefully. Large and co-workers [49–51] have performed the electric field induced (EFISH) experiments in aqueous solutions of DNA and compared the results with the quadratic Kerr effect experiments, done also on DNA aqueous solutions. The studies were made as a function of the average number of base pairs (depending on the

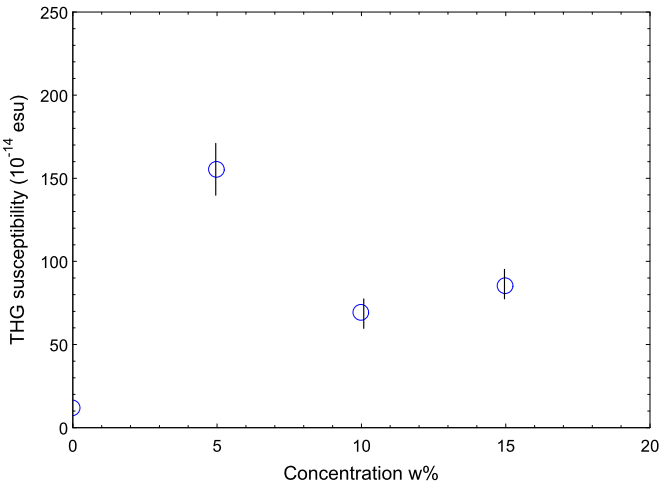


Fig. 4. The observed variation of the THG susceptibility as a function of chromophore concentration in thin films of DNA–CTMA complex, doped with DR1 chromophore.

Fig. 4. La variation observée de la susceptibilité GHT en fonction de la concentration du chromophore dans les films minces du complexe l'ADN–CTMA, dopés avec le chromophore DR1.

molecular mass of DNA macromolecule). The EFISH signal showed a measurable, although not quantified, NLO response from DNA molecule, decreasing with the increasing number of base pairs in DNA, most likely due to the decreasing ability of DNA to orient to the applied electric field. However, these experiments are difficult and their interpretation is not straightforward.

Samoc et al. [52] determined the real and imaginary parts of the nonlinear index of refraction of DNA in solution by wave dispersed femtosecond z-scan technique. They found that it varies between 2×10^{-15} and 10^{-14} cm^2/W in the wavelength range 530–1300 nm. They have reported also an observation of a weak two-photon absorption (TPA) below 600 nm, with nonlinear absorption coefficient equal to 0.2 cm/GW at 530 nm. Apparently it corresponds to the two-photon transition in phenyl rings.

Derkowska et al. [53] have reported the degenerate four wave mixing (DFWM) and nonlinear transmission measurements on DNA–CTMA complex, doped with several complexes, such as DR1, cobalt phthalocyanine (CoPc) and fullerene C_{60}. A different behavior of DFWM susceptibility than when these molecules are dissolved in other solvents was observed, indicating the influence of ionic environment of DNA on embedded chromophores.

We have measured the electronic $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ susceptibility of thin films of DNA–CTMA–DR1 complexes as a function of NLO chromophore concentration (Rau et al. [36]). The observed concentration dependence of THG susceptibility is displayed in Fig. 4. From this figure one can see a large $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ susceptibility value for 5% w/w of DR1 as compared to that of pure DNA–CTMA complex [54]. This susceptibility decreases at 10% and slightly increases at 15%. This behavior is in odds with what we expect from the increase of active molecules density with concentration, $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ being directly proportional to it. To understand and explain this behavior we have performed careful optical absorption measurements of thin films with different DR1 content and we have observed that the charge transfer absorption band is shifting towards the lower wavelengths (higher energies) with increasing chromophore concentration; the shift being associated with its modification (cf. Fig. 5). Such shift can be due to two effects: aggregation and/or intercalation. The interaction aspects of DNA–CTMA complexes with guest molecules were discussed by several authors (see, e.g. Pawlik et al. [55]). In fact DR1 is a small 1-D molecule and can intercalate between CTMA molecules at lower concentration. At higher guest concentration, the doping is expected to be a statistical one. As the environment of DR1 molecule changes, its electronic structure changes too and, as consequence, its optical absorption spectrum. But, as it is seen from Fig. 5, showing schematically the THG process with the observed absorption spectra, an important two-photon resonant contribution to $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ susceptibility is expected at the used fundamental excitation wavelength of 1064.2 nm, as it was the case. So, logically, we expect a change of the THG susceptibility with displacement of the two-photon resonant bands.

In order to demonstrate this we use a simple three level model [56], derived from the quantum mechanical perturbation calculations by Orr and Ward [57]. Within this simplified model (we are not interested in exact values but in the overall dispersion of NLO susceptibilities considered here), the THG susceptibility is given by the following expression (cf. Ref. [56]):

$$\chi^{(3)}(-3\omega;\omega,\omega,\omega) = \frac{NF|\mu_{ng}|^4}{\hbar^3}\left[\frac{|\mu_{nm}|^2}{|\mu_{ng}|^2}\left\{\frac{1}{(\Omega_{ng}-3\omega)(\Omega_{ng}-2\omega)(\Omega_{ng}-\omega)} + \frac{1}{(\Omega_{ng}^*+\omega)(\Omega_{ng}-2\omega)(\Omega_{ng}-\omega)}\right.\right.$$
$$\left.\left. + \frac{1}{(\Omega_{ng}^*+\omega)(\Omega_{ng}+2\omega)(\Omega_{ng}-\omega)} + \frac{1}{(\Omega_{ng}^*+\omega)(\Omega_{mg}^*+2\omega)(\Omega_{ng}^*+3\omega)}\right\}\right.$$

$$-\left\{\frac{1}{(\Omega_{mg}-3\omega)(\Omega_{mg}-\omega)(\Omega_{ng}-\omega)}+\frac{1}{(\Omega_{mg}-\omega)(\Omega_{ng}^{*}+\omega)(\Omega_{ng}-\omega)}\right.$$
$$\left.+\frac{1}{(\Omega_{mg}^{*}+3\omega)(\Omega_{mg}^{*}+\omega)(\Omega_{ng}+\omega)}+\frac{1}{(\Omega_{mg}^{*}+\omega)(\Omega_{ng}^{*}+\omega)(\Omega_{ng}-\omega)}\right\}\Bigg] \quad (1)$$

where $\Omega_{mn}=\omega_{mn}-i\Gamma_{mn}$, with ω_{mn} being the transition energy between states m and n: $\omega_{mn}=(E_m-E_n)/\hbar$ and Γ_{mn} the associated dumping term (cf. Fig. 5). Obviously $\Omega_{mn}^{*}=\omega_{mn}+\mathrm{i}\Gamma_{mn}$. In Eq. (1) N is the molecule density, F is the local field factor and μ_{nm}'s are the transition moment elements between n and m states.

Eq. (1) shows that in a THG process three kinds of resonance enhancements are possible: one-photon ($\omega_{mg}\approx\omega$), two-photon ($\omega_{mg}\approx 2\omega$), and three-photon ($\omega_{mg}\approx 3\omega$). For the computation we have assumed the one-photon level at the already mentioned UV absorption of phenyl rings at 270 nm (three-photon resonance with CT transition band is well beyond the measurement wavelength, in IR, around 1.5 μm) and varying two-photon level position between 510 and 450 nm, as observed experimentally (cf. Fig. 5). As all parameters intervening in Eq. (1) are not known, we made two computations for two values of the square of the dipolar transition moment elements: $R=\frac{|\mu_{nm}|^2}{|\mu_{ng}|^2}=0.5$ and $R=2$, although, as shown by Kuzyk [58] for the linear case, the choice is not completely arbitrarily. The computations were performed for three different values of the dumping term, assumed, for the sake of simplicity, to be the same for both absorption bands: "1-photon" (giving in this case a three-photon resonant contribution) and two-photon. We note that because of the large electric field on molecule the selection rules are broken and one- and two-photon transitions are possible between fundamental and all excited levels as well as between all excited levels. However, such a classification allows us to take into account the most contributing to THG susceptibility two- and three-photon resonances. The results of the computations are shown in Figs. 6 and 7 for three dumping term values: $\Gamma=750, 1500$ and $3000\ \mathrm{cm}^{-1}$ and the already mentioned two values of R. They show that indeed the value of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ susceptibility, in all cases, decreases when the absorption band shifts towards the lower wavelengths, as expected. In both cases the variation depends on the damping term, as expected too. It means that narrower is the "two-photon" band stronger is the of NLO susceptibility dependence on its position.

Although the choice of R parameter does not change the conclusions on the sense of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ susceptibility variation due to the shift of the absorption band, it shows the relative importance of two- and three-photon resonant contributions, depending on it. Thus the observed increase of THG susceptibility, observed in Fig. 7 when approaching 450 nm may be just due to a larger three-photon resonant contribution.

4. Electrical properties

Par excellence DNA is a negatively charged anionic polyelectrolyte, with sodium ions Na^{+} as counter ions. The electric conductivity of DNA was a subject of continuous research interest and of controversy from the early 1960s, [59–61], with

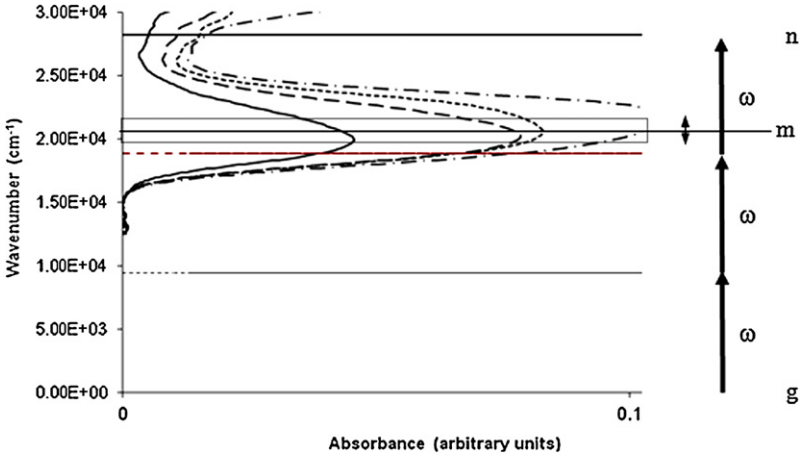


Fig. 5. DR1 chromophore concentration variation of optical absorption spectra of thin films of DNA–CTMA complex (LHS) and schematic presentation of THG process (RHS). The rectangular area as well as the small vertical double arrow show the range of the variation of CT band which contributes to THG susceptibility via a two-photon resonance (taking place with level m). Continuous line refers to 5% w/w concentration. The other curves are for: – – – 10%, ····· 15% and –·–·– 20%, respectively. g, n, m are, respectively, fundamental and excited states of unperturbed system (shown also by solid lines) and dashed lines show virtual states.

Fig. 5. Variation de l'absorption optique des films minces en fonction de la concentration (coté gauche) du chromophore DR1, dissous dans le complexe solide de l'ADN–CTMA et une présentation énergétique du processus de la génération d'harmonique trois (coté droit). La zone rectangulaire indique la plage de la variation de la bande à transfert de charge du chromophore, qui contribue essentiellement à la susceptibilité cubique par l'intermédiaire d'une résonance à deux photons. La ligne continue se réfère à 5% w/w de la concentration du chromophore. Les autres courbes correspondent, respectivement, à : – – – 10%, ····· 15% et –·–·– 20%. g, n, m sont, respectivement, le niveau fondamental (g) et les niveaux excités (n, m) du système non perturbé (montrés également par les lignes continues) et les lignes en pointillés indiquent les niveaux virtuels.

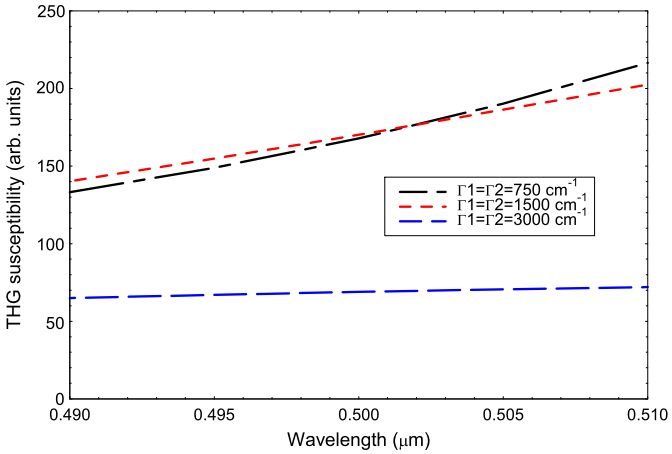


Fig. 6. Wavelength variation (within the CT band shift) of the THG susceptibility, computed within the three level model, for the parameter $R = 0.5$ and for three different values of damping terms Γ_1 and Γ_2 ($\Gamma_1 = \Gamma_2$, for details see the text).

Fig. 6. Variation de la susceptibilité cubique de génération d'harmonique trois en fonction de la longueur d'onde (dans la bande déplacement de la bande à transfert de charge), calculée dans un modèle à trois niveaux, pour le paramètre $R = 0{,}5$ et pour trois différentes valeurs de termes d'amortissement Γ_1 and Γ_2 (pour plus de détails voir le texte).

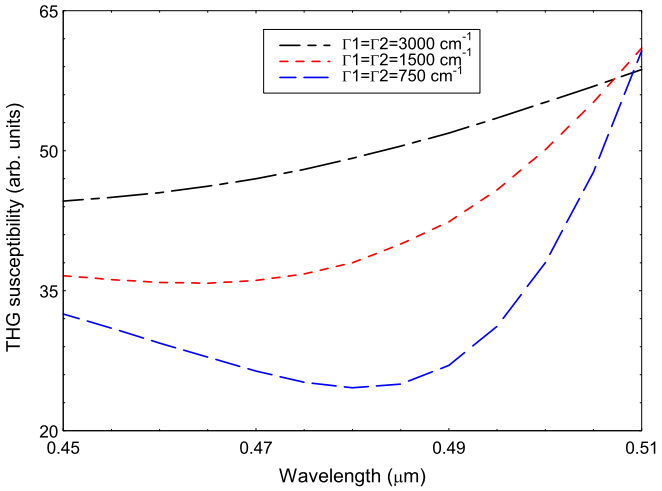


Fig. 7. Wavelength variation (within the CT band shift) of the for THG susceptibility, computed within the three level model, for the parameter $R = 0.5$ and for three different values of damping terms Γ_1 and Γ_2 ($\Gamma_1 = \Gamma_2$, for details see the text).

Fig. 7. Variation de la susceptibilité cubique de génération d'harmonique trois en fonction de la longueur d'onde (dans la bande déplacement de la bande à transfert de charge), calculée dans un modèle à trois niveaux, pour le paramètre $R = 2$ et pour trois différentes valeurs de termes d'amortissement Γ_1 and Γ_2 (pour plus de détails voir le texte).

the first theoretical suggestion by Eley and Spivey [62] that the delocalization of π electrons in nucleobases may lead to an efficient electron transport along the DNA stacks [63].

The DNA conductivity measurements performed by different research groups show insulating to superconducting behavior [64–69]. Fink and Schonenberger [70] have reported the transport of electric current by DNA as efficient as that of a good semiconductor. This observation was later confirmed by Kasumov et al. [68]. It contradicts the findings by Porath et al. [71] and De Pablo et al. [66]. They report a very poor DC conductivity in this biopolymer. The controversy about the conductivity was cleared out very recently by Genereux et al. [60,72]. They argue that its true mechanism is the charge transfer along the π-stacks of the bases, as it was initially proposed by Eley and Spivey [62]. The peripheral part of DNA molecule with sugars and phosphates behaves essentially as an insulator. Therefore, depending how the conductivity measurements are done, i.e. how the measurement apparatus is "connected" to DNA, different conductivity results are obtained.

The polyelectrolyte properties of DNA are more pronounced when dissolved in water because of the presence of mobile bulk ions, some of them forming condensed and diffuse counter ions [73]. As DNA is water soluble, it is possible to obtain the samples in the thin film form by solution casting technique. As it was shown by Pawlicka et al. [74] DNA can

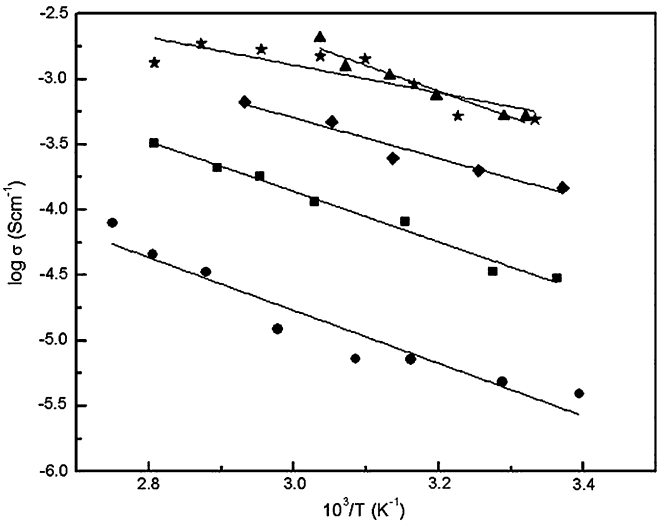


Fig. 8. Ionic conductivity, in logarithmic scale, as a function of inverse temperature (in K) for selected membranes: DNA–glycerol (●) (lower glycerol content), DNA–glycerol (■) (higher glycerol content), DNA–glycerol:$LiPO_4$ (◆), DNA–PEDOT:PSS (▲), DNA–glycerol:PB (★) (adapted from [74,75]).

Fig. 8. La conductivité ionique, en fonction de l'inverse de la température (en K) pour les membranes sélectionnées : ADN–glycérol (●) (faible teneur en glycérol), ADN–glycérol (■) (teneur élevée en glycérol), ADN–glycérol:$LiPO_4$ (◆), ADN–PEDOT:PSS (▲), ADN–glycérol:PB (★) (adapté de [74,75]).

be plasticized with glycerol allowing obtaining of a processable material and fabrication (for details see Refs. [32,33]) of transparent membranes (in visible) with good ionic conductivities.

We have prepared and studied a series of DNA based materials for fabrication of conducting membranes and for application in electrochromic cells [32,33,75]. The membranes were prepared from solution in water of DNA and glycerol as plasticizer. Other ionic doping molecules to increase the electrical conductivity were also used, as specified below. The obtained viscous solution was poured in Petri dishes and let to dry for a few days at 40 °C in a dry box. Depending on the concentration and the amount of solution used as well as the diameter of Petri dish free-standing membranes with thickness ranging from 0.01 to 0.5 mm were obtained. After preparation the membranes were stored in a dry box.

The measurements of electrical conductivity were performed on the cut round pieces of the studied membranes, with diameter of 2 cm, pressed between two stainless steel electrodes. The system was installed in a glass cell under vacuum and the measurements were performed with Solartron 1260 apparatus. The conductivity measurements were performed in function of temperature, what allows one to check its ionic, or not, character.

As already mentioned, to increase the electrical conductivities the membranes were additionally doped with lithium perchlorate ($LiClO_4^-$), Prussian Blue ($K[Fe^{III}Fe^{II}(CN)_6]$) (PB) and a well known conducting polymer PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)). The observed temperature variations of the ionic conductivities of studied membranes, in the temperature range of 24–83 °C, are shown in Fig. 8. All membranes, except DNA–glycerol:PB complex, exhibit similar behavior, with similar activation energies, which can be described by an Arrhenius dependence (solid lines in Fig. 8). The observed departure from linear dependence for DNA–glycerol:PB complex is interpreted as being due to the ionic motion, coupled to the segmental motion of the polymeric chains [76].

For the pure DNA–glycerol membranes already adding more of the plasticizer to DNA results in an increase of the ionic conductivity as shown in Fig. 8 (two lowest curves: full circles – lower DNA content or high glycerol content and full squares – higher DNA content or lower glycerol content). However there are limits for glycerol concentration to obtain solid membranes, which have to be respected, as this compound is liquid at room temperature. The ionic conductivities in these two studied cases range from 3.9×10^{-6} S/cm at 22 °C and 7.9×10^{-5} S/cm at 90 °C for the low DNA and 3×10^{-5} S/cm at 24 °C and 3.2×10^{-4} S/cm at 83 °C for high DNA content.

Doping with $LiClO_4$, PEDOT:PSS and PB increase substantially the membrane conductivities, by more than two orders of magnitude with respect to DNA–glycerol samples. The best, and very similar, results are obtained for DNA–glycerol: PEDOT:PSS and DNA–glycerol:PB. In the first case the observed ionic conductivity increases from 5.1×10^{-4} S/cm at 28 °C to 2.1×10^{-3} S/cm at 56 °C. For DNA–glycerol:PB membranes the ionic conductivity varies between 5×10^{-4} S/cm at 27 °C and 1.3×10^{-3} S/cm at 80 °C. Doping with $LiClO_4$ gives membranes with conductivities varying between 1.5×10^{-4} S/cm at 23 °C and 3.6×10^{-4} S/cm at 68 °C (diamond symbols).

5. Applications

Several practical applications of DNA in photonics and in electronics were already demonstrated. As already mentioned DNA–CTMA, due to its tunable conductivity by controlling molecular mass of DNA, is a choice material for buffer layers in EOMs [18,23]. Czaplicki et al. [77] have shown the formation of a refractive index grating in DNA–CTMA thin films doped

with DR1 chromophore. On the contrary to the case when the gratings (called also surface relief gratings (SRG) due to the mass transportation induced by light) are formed by mass transport of both chromophore and polymer, in these cases no SRG was observed. Most likely in that case only chromophores are displaced. This behavior is due to the large free volume in DNA, as compared with synthetic polymers.

DNA appears also as an interesting matrix for luminophores. Several papers report a significant increase of photoluminescence efficiency in DNA matrix, as compared to other matrices (see e.g. Ref. [78]). As already mentioned, a few practical applications of DNA–CTMA complexes doped with luminophores were already demonstrated. Hagen et al. [79] presented results of improvement of the electroluminescent properties of BioLEDs by using DNA–CTMA complex as an electron blocking layer [80,81]. Very recently Kobayashi and co-workers have demonstrated an electric field steered, large emission wavelength range of a DNA based BioLED with AlQ_3 and $Ru(bpy)_3^{2+}$ as active molecules [82,83]. Moreover, it was shown that DNA can be used as a super capacitor, with variable and controllable capacity [84].

DNA–CTMA complex is also an interesting matrix for lasing [85–87]. Amplified spontaneous emission (ASE) was observed by several research groups [86,88–90] (for a recent review see Ref. [91]). In particular Mysliwiec et al. [92] have observed ASE from MR isomer of spiropyran embedded in DNA–CTMA matrix. This effect is not observed when using synthetic polymers as matrix, such as, e.g. polymethyl methacrylate (PMMA). A two-photon lasing was also demonstrated in a DNA–CTMA:chromophore complex [93].

Other interesting effects were also observed in holography experiments with thin films of DNA–CTMA, doped with photoactive molecules such as DR1 and Disperse Orange 3 (DO3). Both molecules photoisomerize under light illumination and the process is associated with a large refractive index variation. For practical applications, the refractive index grating writing and decay times are important. When doping with DR1, these were found to be of a few milliseconds [94], i.e. four orders of magnitude shorter than in the case of PMMA matrix [92]. For the second azodye DO3 the response time, measured with a pulsed, nanosecond laser [95], was found even two orders of magnitude faster (a few tens of microseconds), as compared with DR1 case. Here the peculiar structure of DNA and the large free volume are believed to be behind this short response time.

Very interesting applications are expected from exploiting the electrical properties of DNA based processes. As already mentioned it was shown very recently that DNA can be used as a super capacitor, with variable and controllable capacity [84]. We have demonstrated use of the DNA based membranes in smart windows. Under the applied electric field the transmission of such windows changes from 43% to 27% at 600 nm for the electrochromic device with WO_3/DNA–PEDOT:PSS/CeO_2–TiO_2 composition [33,74]. The interesting fact here is that the DNA based electrolytes are obtained as solid, free standing films, what facilitates greatly technologies for their practical applications.

Another potential field of applications of DNA based materials are chemical sensors as shown by Yaney et al. [96].

6. Conclusions

Deoxyribonucleic acid (DNA) is an abundant, renewable, biodegradable and natural macromolecule. It can be obtained from the waste produced in food processing industry. That used in our studies originates from the waste produced in fish processing. Thus it can be cheap and the renewable resources are practically unlimited. Owing to its peculiar double stranded helical structure it can be used as a matrix for photosensitive and charge transporting molecules, offering an interesting, ecologically friendly, alternative material for applications in photonics and in electronics.

DNA can be functionalized with surfactants, leading to a temperature stable material, processable into good optical quality thin films by solution casting techniques. The structure of DNA and the ionic environment it offers changes the physico-chemical properties of embedded active molecules in a favorable way as shown and discussed in this paper. Different doping mechanisms were indicated. The richness of the possible functionalization of DNA gives possibility of obtaining an important class of materials with new properties and new functionalities. They may be cheap, as obtained from the waste produced in the food processing industries and environmentally friendly, as already mentioned. As photoactive materials natural chromophores, like anthocyanins, can be, perspectively, used too [97]. We note too that the liquid crystalline phase was also isolated in DNA and investigated [86,98] as well as in a DNA–surfactant complex [99].

The observed anomalous variation of THG susceptibility as a function of concentration in thin films of DNA–CTMA complex, doped with DR1 chromophore, is tentatively explained by the observed shift of the CT absorption band, within the quantum three level model. As argued, the shift may be due to intercalation, aggregation or to both.

The research on optical and electrical properties, not only of DNA but on other biopolymers, although growing rapidly, is still at its infancy and requires further efforts. Our study and other recent studies on DNA show a high potential of this material for practical applications. It can be functionalized with active molecules to provide required properties for a number of applications in electronics and in photonics. The peculiar double stranded helical structure provides a large free volume for doping molecules, allowing faster conformational transformations of photochromic molecules, as discussed here. Moreover, a significantly slower thermal and photochemical decay of photoactive polymers, embedded in DNA–CTMA matrix, as compared with synthetic polymers [5,6] is also in favor of biopolymers as well as the high optical damage threshold. Our studies show also a higher concentration limit for aggregation, most likely due to the “protective” role of the helix. It allows obtaining more efficient materials, with higher chromophore concentration, for NLO and OLED applications.

As it is discussed in this paper the electrical conductivity of DNA can be tailored by doping. In the specific case we obtained and increase of conductivity by more than two orders of magnitude (cf. Fig. 8), by choosing appropriate dopants.

These values can be still improved. Moreover, the doped DNA can be easily transformed into solid electrolyte, which can find a lot of applications, not only in electrochromic displays, smart windows as we have shown, but also in solar energy conversion, batteries, etc.

Grote et al. [35,100] have shown application of DNA–CTMA as buffer layers in electro-optic modulator. It exploits the good optical beam propagation properties on one side and the tuneable resistivity of DNA–CTMA complex, which depends on its molecular mass. Having the buffer layer of lower resistivity than that of active layer leads to a better electric field distribution in the EOM structure, and thus more favorable operation conditions.

Another, not the last argument in favor of using biopolymers is their origin. DNA used in our studies is extracted from the waste in fish processing industry. It can be cheap and the renewable resources are practically unlimited. Moreover DNA is biodegradable, what is an important advantage in the planned creation of sustainable society with durable development.

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