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Biopolymer Thin Films for Optoelectronics Applications

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Nowadays one observes a growing interest in studying and application of ''green materials'' – biomaterials. For an appropriate use of them in practical devices a good knowledge and understanding of their properties are necessary. This paper presents some results obtained for two, the most abundant on the Earth, biopolymers which are DNA and collagen. In order to make these biopolymers useful they have to be functionalized with active molecules, bringing them a researched property. The biopolymers were doped with Rhodamine 590 and Disperse Red 1. The contact angle measurements are also presented and discussed. The present studies show that the properties of these materials depend on the dyes used to render them optically responsive in visible range and on the biopolymer as well. They show that interaction with substrate is modified by the added dye, as expected. We have measured also the optical damage threshold of studied biopolymers at 1,064 nm and we found that it is about one order of magnitude higher for the studied biopolymers as compared with the synthetic ones.

Keywords AFM; biopolymer; collagen; contact angle; DNA; optical damage threshold

Introduction

In recent years the scientists have turned increasingly their attention to the intricate and beautiful nature of biological systems. An explosion of new experimental techniques that probe and manipulate complex biological materials at the molecular level has allowed quantitative measurements of properties that were previously the subject of speculation. Researchers are particularly interested in exploring the physical properties of biological systems and biologically important molecules, such as e.g., DNA. They use some techniques to measure the local electrical and structural

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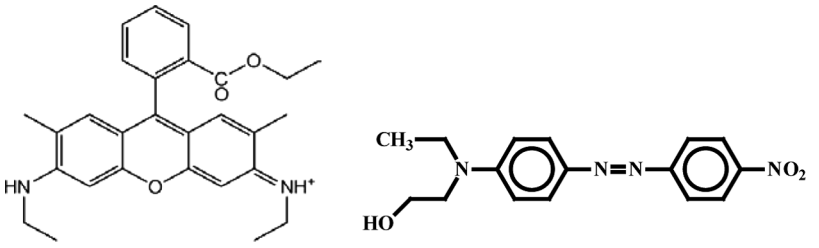

(a) (b)

Figure 1. Chemical structures of Rhodamine 590 (a) and Disperse Red 1 (b).

properties of self-assembled monolayers of these molecules. Their results feed back into investigations of the optical properties of these materials, and reveal how the molecules can be engineered to create a new class of designed practical biomaterials [1–4]. Apart from their potential relevance to biology, the study of these systems has revealed new physical phenomena characteristics of the highly-fluctuating sub-micron world (nano-world).

Materials and Apparatus

Thin films were obtained by spin coating of solutions of studied compounds on the carefully cleaned glass substrates. Spectroscopic grade solvents were used. The spin coating machine was Laurell – Model WS – 400B – 6NPP/LITE. As compounds we used commercially available Rhodamin 590 (Exciton) and Disperse Red 1 (Aldrich). The dyes were additionally purified by recrystallization and liquid chromatography. DNA was obtained from salmon waste in Chitose Institute of Science & Technology, Japan and the collagen was obtained from bovine derma in National R&D Institute for Textile and Leather, Division ICPI – Collagen Dept., Romania. Figure 1 shows the chemical structure of the used dyes.

DNA was functionalized with CTMA in order to improve the physico–chemical properties of material [5]. The guest-host systems at different concentrations of dye molecules were prepared in an appropriate solvent solution (bidistilled water for collagen and buthanol for DNA-CTMA).

Results and Discussion

Spectral Analysis

All studied thin films were characterised by the UV-VIS-NIR spectrometry. Indeed, we know that for optoelectronic applications the materials should have no absorption, particularly in the telecommunications windows (1300–1500 nm). For local area networks (LAN) with polymer fibers important is also transparency in the red part and near IR (600–800 nm) [6]. Thus the knowledge of the absorption spectrum allows to determine the operation wavelength range. On the other hand, even when working in IR the presence of absorption band may lead to multiphoton absorption and as consequence large propagation losses excluding use of material even in transparency range. It is particularly the case for two photon absorption (TPA), which occurs at double of the one photon absorption wavelength for noncentrosymmetric

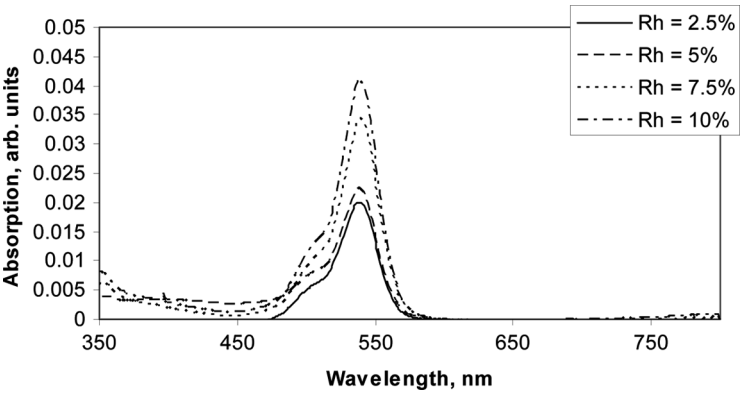

Figure 2. Optical absorption spectra of collagen thin films with different concentrations of Rhodamine 590 (Rh). The spectra are not normalized to the thin film thicknesses.

molecules. The case of centrosymetric molecules is more complex, as a two photon level may lie in the material transparency range. Also, in e.g., harmonic generation experiments it is necessary to correct the generated harmonic intensities for chromophore absorption at harmonic wavelength. The optical absorption spectra of studied thin films were recorded in transmission mode using a JASCO UV-VIS-NIR spectrophotometer, model V 670 spectrometer.

From Figure 2 one can see that the optical absorption spectra recorded for Collagen–Rhodamine 590 thin films are similar in shape for four studied concentrations, no matter the chromophore concentration (up to 10% of rhodamine). Similar behaviour is observed for DNA-CTMA-Rhodamine with 10 and 20% of chromophore (cf. Fig. 3). It means that in both cases no modification of the electronic structure of guest molecule takes place. Note, that the absorption spectra were not normalized to the thin film thicknesses, so the optical densities don't match with the chromophore concentrations, as we were interested only in the shape of the absorption band (wavelength dependence).

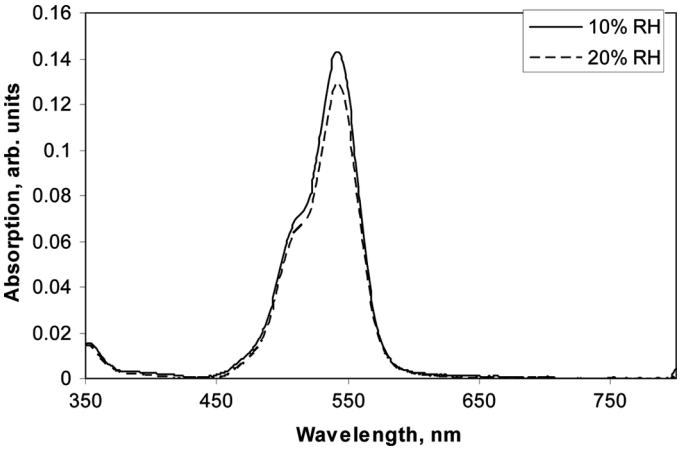

Figure 3. Optical absorption spectra of DNA-CTMA thin films with different concentration of Rhodamine 590 (Rh). The spectra are not normalized to the thin film thicknesses.

In contrast, a strong modification of the absorption band of DR1 dissolved in DNA-CTMA matrix is observed with increasing chromophore concentration. For two low concentrations of DR1: 5% and 10% of DR1 the absorption spectra are very similar, with the maximum absorption wavelength λ_{max} of around 500 nm (cf. Fig. 4) while for a high concentration of DR1 (15% and 20%) the shape of adsorption spectra is changed. Such effect, known in literature as solvatochromic effect is observed when the polarity of chromophore environment is changed and is due to the DC Stark effect. So these observations show that there are two types of environment of DR1 molecule. It can be explained in terms of already mentioned semiintercalation. At low chromophore concentration the DR1 molecules could intercalate into the DNA helix. After a certain concentration of DR1 there is no more room inside the helix and the chromophores rest outside the helix. This kind of "intercalation" was also observed by Mitus and Mysliwiec in their theoretical studies, and they called it "semiintercalation" (oral presentation at International Conference on Functional Materials and Devices – Kuala Lumpur, June 2008). The fact we do not observe it for rhodamine can be explained by its size. This molecule is larger (in diameter) than DR1 and because of that the intercalation is impossible. The "protective" environment of intercalated molecules make them also more resistant to degradation, as it was observed (cf; Ref. [7]) and their decay time is larger.

Figure 5 shows the absorption spectra of thin films of collagen doped with DR1. One observes a strong modification of the absorption band with respect to the DNA-CTMA matrix and low concentration. Two absorption bands are observed: a broad one at around 520 nm, red shifted with respect to that of DNA-CTMA-DR1 and a second one, with λ_{max} of about 400 nm. For all concentrations both bands are present with their relative intensities almost constant. Broadening of the absorption band at 520 nm is due, most likely, to the inhomogenous environment of DR1 chromphore. The band at 400 nm may come from the aromatic rings, which appear after the breaking of the nitrogen double bond $-N{=}N-$.

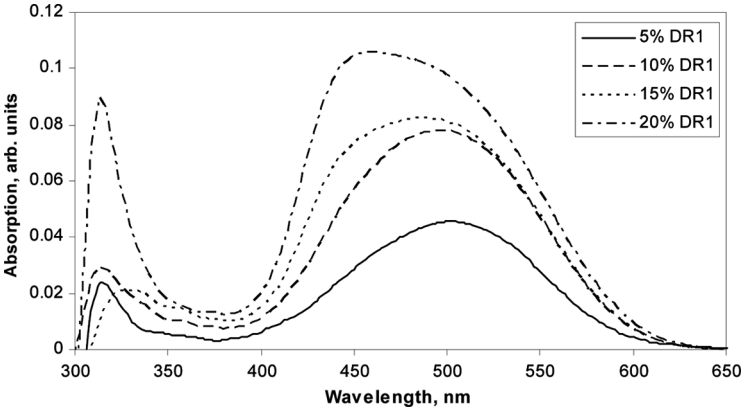

Figure 4. Optical absorption spectra of DNA-CTMA thin films with different concentration of Disperse Red 1 (DR1). The spectra are not normalized to the thin film thicknesses.

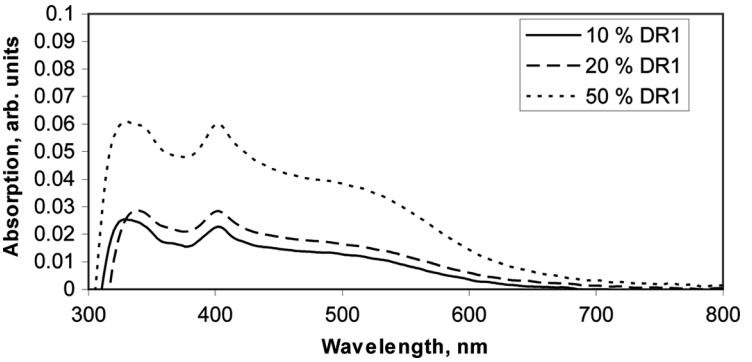

Figure 5. Optical absorption spectra of collagen thin films with different concentrations of Disperse Red 1 (DR1). The spectra are not normalized to the thin film thicknesses.

AFM Investigations

The thin film surface studies were performed with a Digital Instruments multimode Nanoscope III atomic force microscope (AFM) operated in contact or noncontact mode. Figure 6 shows the AFM images of thin films made of DNA-CTMA-DR1 solutions with different chromophore concentrations. It can be seen that for the low dye concentration only very small and isolated aggregates are present. With increasing chromophore concentration these aggregates grow in height, length and in width. At higher concentration (20% DR1) the aggregates are covering practically the whole thin film surface. The aggregation is a well known phenomenon of dipolar molecules (see e.g., [8]).

Figure 7 shows AFM images of a collagen based thin film, doped with DR1. The images were recorded immediately after the thin film preparation. Although the chromophore concentration is high (20%) there are no aggregates as it can be seen from the Figure 7a so the dye is dispersed in the collagen matrix. Moreover the phase image (Figure 7b) confirms this hypothesis and suggests creation of a network during the film preparation; a network with the pitch of about 1 μm.

Contact Angle Measurements

We have also performed the contact angle measurements on studied materials using a KSV Instruments commercial apparatus, model CAM 100. The measurements

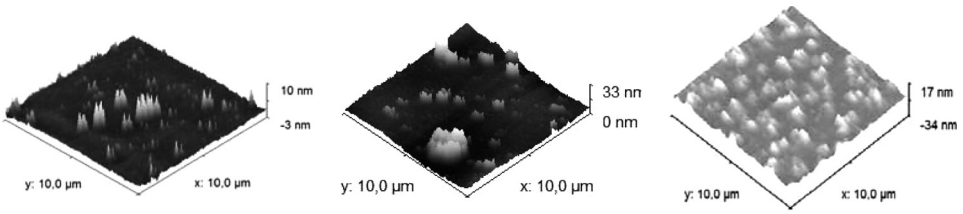

Figure 6. Topographic 3D AFM images for DNA-CTMA based films with 5% DR 1 (a), 10% DR1 (b), and 20% DR1 (c).

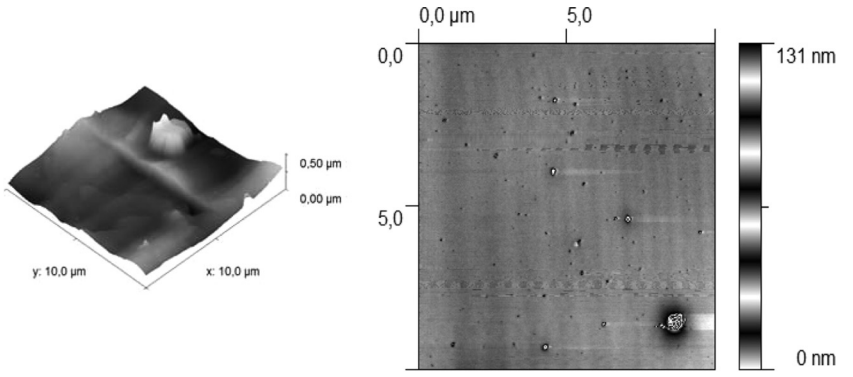

Figure 7. AFM images for collagen based films with 20% DR1: topographic 3D image (a) and 2D phase image (b).

were performed on thin films. They give information about the strength of intermolecular interactions in studied material with respect to those with substrate. The results obtained from these measurements are given in Tables 1 and 2. It is seen that the largest contact angle is observed in the case of DNA-CTMA-Rhodamine thin films. The contact angle depends on chromophore concentration for the films with rhodamine while the variation of the contact angle for material doped with DR1 is almost independent on the chromophore concentration in the studied range.

Optical Damage Threshold

Optical damage threshold is another important parameter determining the utility of a given material for application in nonlinear optics where usually light beams with very high intensity are used. It was measured for the studied thin films using the experimental set-up shown in Figure 8. The measurements were performed at 1064.2 nm wavelength with a Q switched Nd: YAG laser. The pulse duration was

Table 1. Contact angle measurements for the DNA-CTMA based thin films

Thin film material	DNA-CTMA-Rh 10%	DNA-CTMA-Rh 20%	DNA-CTMA-DR1 5%	DNA-CTMA-DR1 10%	DNA-CTMA-DR1 15%	DNA-CTMA-DR1 20%
Contact angle [degrees]	58.87	74.12	65	66	68	69

Table 2. Contact angle measurements for the collagen based thin films

Thin film material	Collagen-DR1 10%	Collagen-DR1 20%	Collagen-DR1 50%	Collagen-Rh 5%
Contact angle [degrees]	52	53	54	45

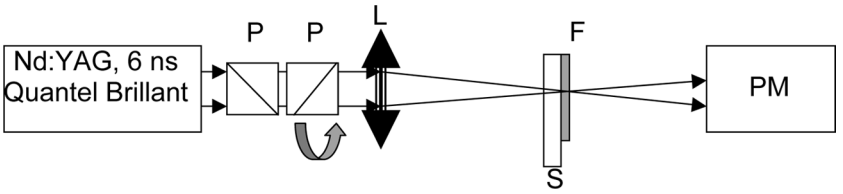

Figure 8. Schematic presentation of experimental set-up optical damage threshold measurements.

of 7 ns. The studied film was kept in focus of the focusing lens. Single shots were used only, varying the incident intensity with a system of two polarizers. By rotating the second polarizer a monotonic and well controlled intensity variation of the incident beam on the sample is obtained. The obtained results are collected in Table 3 while Figure 9 shows, as an example, the speckles created after the illumination of thin films at the damage threshold. The results show that the DNA-CTMA based films

Table 3. Results of optical damage threshold experiment

Film	P-damage, W/m^2	P-damage, GW/cm^2
DNA-CTMA-DR1–5%	3.3372E + 13	3.3372
DNA-CTMA-DR1–10%	3.6178E + 13	3.6178
DNA-CTMA-DR1–20%	4.7922E + 13	4.7922
DNA-CTMA	5.1913E + 13	5.1913
DNA	5.2647E + 13	5.2647
Collagen	4.1387E + 13	4.1387
PC	2.9805E + 12	0.29805
PEG	7.8092E + 12	0.78092

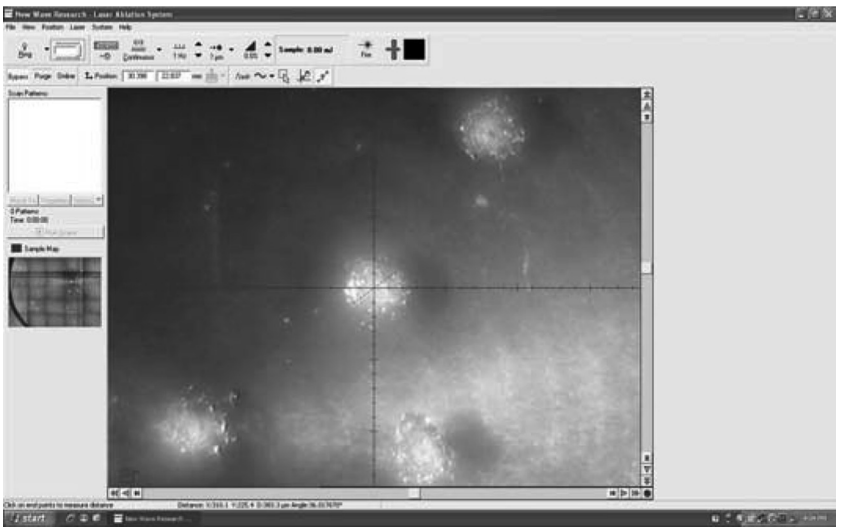

Figure 9. Optical microscope pictures of speckles created in thin film at high laser beam fluencies.

exhibit about one order higher optical damage threshold than the films based on synthetic polymers: polycarbonate (PC) and polyethyleneglycol (PEG). It is a very interesting result showing that the biopolymers withstand higher light fluencies than the synthetic ones. The optical damage thresholds of collagen and DNA-CTMA films are very close. Surprising is the slight increase of damage threshold of DNA CTMA with increasing DR1 concentration. This may be due to the already discussed doping mechanism.

Conclusions

The present study shows the following:

- In the case of DNA CTMA DR1 films the optical absorption spectrum depends strongly on the chromophore concentration, in contrary to the DNA CTMA Rhodamine thin films where such a dependence is not observed. This result is tentatively interpreted by different doping mechanisms in both materials: semliintercalation in the first one and statistic doping in the second.
- The optical absorption spectra recorded for collagen based thin films depend on chromophore. In the case of rhodamine the characteristic chromophore absorption band (at 500 nm) is present and does not change with dye concentration. For collagen films doped with DR1 the chromophore absorption band (around 500 nm) is red shifted and broaden. Another absorption band, around 400 nm is observed, which may be due to the chromophore transformation during the material preparation.
- The AFM images reveal, as expected, that in the case of DNA-CTMA based thin films, doped with DR1, the chromophore aggregates on the thin film surface. The size of aggregates increases with the dye concentration. No aggregates are present in collagen based films with the same chromophore. A possible network formation in that case takes place.
- The contact angle measurement show that doping with Rhodamine leads to the increase of thin films hydrophilicity, increasing also with the dopant concentration. No such effect is observed in the case when doping the biopolymer based thin films with DR1 chromophore.
- The optical damage threshold for studied biopolymer thin films is about one order of magnitude larger than for the two synthetic polymers investigated too: polycarbonate and power for is increased with about one order of magnitude for biopolymer based thin films compared to synthetic polymer thin films.

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