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SPIE.

Event: SPIE Photonics Europe, 2018, Strasbourg, France

Fluorescent properties of nanodiamonds in result of interactions of nanodiamonds with biomacromolecules in water

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ABSTRACT

In the present work an influence of interactions between detonation nanodiamonds and biomacromolecules (DNA and lysozyme) on fluorescent properties of nanodiamonds was studied. Formation mechanisms of complexes of nanodiamonds with DNA and lysozyme molecules were investigated. It was found that fluorescent intensity of detonation nanodiamonds changes in different ways for nanoparticles with different surface composition. It was established that fluorescent intensity of nanodiamonds increases in case of the interaction with a sufficient number of biomacromolecules.

Keywords: nanodiamonds, fluorescence, biomacromolecules, DNA, lysozyme.

1. INTRODUCTION

At the present, there is an active search for novel nanomaterials for the role of theranostic agents for the biomedicine, which would meet such requirements as nontoxicity, photostable fluorescence, abilities to be easily suspended and to reliably hold drugs on their surface[1]. Various carbon nanoparticles are fulfilling these requirements to varying degree, and between them nanodiamonds (NDs) stand out[2-5]. Nanodiamonds are known for their stable fluorescence, low toxicity to cells and a complex polyfunctional surface that in many ways determines properties of NDs in suspensions and biological systems. The surface can be further modified and hybridized by various chemical groups and polymers with following attachment of various drugs. Such capacity for surface modification of NDs allows to give them the desired properties needed for the solving of the particular problems of nanomedicine – disease diagnostics, drug targeting, high adsorption selectiveness and others[4-7].

The possibility of ND's surface to be differently functionalized determines the high adsorption properties of these nanoparticles to various substances: to ions and nitrates of heavy metals[8], to viruses[9], to molecules of DNA[10,11], to proteins[12-14], to various drugs[15-20]. Many authors showed that adsorption properties of NDs are dependent on their ζ-potential and type of surface groups[8,21]. For example, authors of [8] in the result of comparative analysis of adsorption properties of NDs with different surface functionalization found that adsorption properties of NDs with carboxylic surface groups –COOH are several times higher than that of the NDs with the polyfunctional surface. Authors of [11] determined that carboxylated NDs are adsorptively selective to the different forms of DNA chains: linear forms of DNA can be adsorbed when circular forms cant. In papers [12-14] it was shown that through the physical adsorption such proteins as cytochrome C, lysosomes, lysozyme can be adsorbed on the surface of carboxylated nanodiamonds. As well, it was shown that through electrostatic interaction many drugs can be firmly adsorbed on the surface of ND-COOH[15-20]. Discovered adsorption properties of ND-COOH allowed a creation of fluorescent complexes of NDs with biomacromolecules (proteins-ferments) or drugs for their targeted delivery and therapy of sick cells or organs. To date, the high anticancer efficiency of complexes of NDs with doxorubicin was shown[15-18]. Authors of paper [19] suggest using NDs with carboxylic surface groups as a basis for delivering of insoluble in water purvalanol A for the treatment of liver cancer and of a new drug 4-OHT for the treatment of breast cancer. In paper [21] complexes of ND-COOH with epirubicin – actively used cure for cancer in modern medicine – were successfully approbated on the living mice.

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Biophotonics: Photonic Solutions for Better Health Care VI, edited by Jürgen Popp, Valery V. Tuchin, Francesco Saverio Pavone, Proc. of SPIE Vol. 10685, 106853E

In the development of drug carriers, it is important to be able to track a complex carrier-drug. In case of complexes on the base of NDs this can be done via their fluorescence. The fluorescence of not-doped nanodiamonds originates from their surface – surface defects and oxidic surface groups [22]. However, there exists a number of papers that show that fluorescent properties of NDs are changing not only with functionalization of their surfaces[23,24], but also with changing of their environment[25-28]. In papers [25-27] it is shown that fluorescence of detonation nanodiamonds (DNDs) essentially depends on the polarity of the solvent in which DNDs placed. It was found that with the decreasing of solvent polarity, the fluorescence of NDs intensifies. Unfortunately, there are too few papers devoted to studying of the influence of adsorbed on ND's surface biomacromolecules and drugs on fluorescent properties of NDs themselves. Authors of [14,28,29] showed that fluorescence of complexes of DNDs and proteins increases compared to the fluorescence of initial DNDs. Besides, it was shown that the fluorescence of complexes with bigger carriers increases more. Authors [28,29] explain these results by the transfer of energy between diamond- and graphite-like structures and adsorbed protein molecules. In the case when a characteristic size of nanocluster is smaller than the effective size of the wave function of an excited electron, such an electron can freely interact with the nearest environment of the nanocluster – with diamond core or adsorbed protein.

In this paper, the results of a study of the influence of adsorbed molecules of DNA and lysozyme (Lys) on the fluorescence of DND-COOH are presented. Complexes DND+DNA and DNA+Lys have the wide prospects in their use as sensors and antibacterial drugs, accordingly.

2. METHODS

Zeta-potential of DNDs suspensions in the presence of surfactant was measured using Malvern ZetaSizer NanoZS (Malvern, Worcestershire, UK).

The sizes of DNDs in the suspensions were investigated by **dynamic light scattering (DLS)** at the correlator-goniometer system ALV-CGS-5000/6010 (Langen, Germany) equipped with a He-Ne laser (wavelength 633 nm; radiation power of 20 mW).

Spectra of **IR absorption** were obtained using Varian 640-IR FTIR spectrometer (resolution 2 cm^{-1}, ATR attachment with the diamond crystal). Before measurements samples were dried out from the initial suspensions on the ATR crystal by the hot air.

Fluorescence spectra of studied suspensions were recorded on a Thorlabs CCS200 compact spectrometer under the laser excitation of a wavelength 405 nm (power on the sample 100 mW) in the 90° scheme of the experiment. To suppress the scattering at an unshifted frequency, a notch-filter (Edmund Optics) was used. The temperature during the experiment was maintained at 24 °C.

Raman scattering (RS) of ND suspensions was excited by an argon laser with a wavelength of 488 nm and power of 200-400 mW. Integral RS spectra were recorded using the registration system consisted of the monochromator (Acton 2500i, focal length of 500 mm, grating of 900 gr mm^{-1}) and the CCD-camera (Horiba Jobin Yvon, Syncerity-1024x256-OE) in the 90° scheme of the experiment. The width of the entrance slit was 25 μm, which provided the spectral resolution of 1.5 cm^{-1}. Raman spectra were recorded in the range 400-4500 cm^{-1}.

The **absorption spectra** of ND suspensions were obtained on a Shimadzu UV-1800 spectrophotometer with the spectral resolution of 0.5 nm.

pH of the suspensions was determined using the Ionometric converter Akvilon I-500 (Russia).

3. MATERIALS

Hen Egg White **Lysozyme** from Amresco was used**.**

Deoxyribonucleic acid sodium salt from calf thymus (Sigma) was used as a DNA sample.

The initial DNDs were synthesized by the detonation of a mixture of trinitrotoluene and 1,3,5- trinitrotoluene-1,3,5-x-triazine in media with water cooling ("New Technologies", Chelyabinsk, Russia). The further purification from soot and treatment of DNDs were performed at Adámas (Raleigh, North Carolina, USA). For this work, the DNDs functionalized by the carboxylic groups with the sizes of 10 nm (DND 10 nm) and 5 nm (DNDs 5nm) were used. The procedures of DNDs synthesis and purification were described in details in [26,30]. It should be noticed that DND 5 nm and DND 10 nm were treated differently, as a result, DND 5 nm have much more intensive fluorescence due to the production of tiny carbon dots on DND surface[31].

4. RESULTS AND DISCUSSION

4.1 Samples characterization

To prepare samples, the initial substances (DND 5 nm, DND 10 nm, DNA, Lysozyme) were suspended in the deionized bidistilled water (electrical conductivity of 0.1 μSm cm^{-1}) with the concentrations of 8, 28, 6 and 5 g/L accordingly. By the addition of minuscule volumes of Sodium hydroxide NaOH these suspensions were brought to the physiological pH value 7.

Initial suspensions of DND were characterized by their size as well as their ζ-potential. Measurement on the DLS instrument and on the zetasizer showed that the dynamic size of NDs and their ζ-potential for DND 5 nm equal to 5±1 nm, -44.6±4.3 mV, for DND 10 nm – to 10±1 nm, -40.8±2.3 mV.

For the characterization of surface groups of nanodiamonds, the IR absorption spectra of DND 5 nm and DND 10 nm were obtained (Figure 1). The spectra contain bands of stretching (2800-3700 cm^{-1}) and deformation vibrations (maximum at 1630 cm^{-1}) of water O-H groups. In spectra of both DNDs the ester/ketone C=O band (maximum at 1780 cm^{-1}) is well defined, its position indicates the strong oxidation of the diamond surface[32]. The line with the maximum at 1410 cm^{-1} presumably belongs to the vibrations of CH_2 groups[33]. This line is well defined in the spectrum of DNDs 5 nm but is absent in DNDs 10 nm. In the spectrum of DND 5 nm, the line at the region of 1274 cm^{-1} is present, which supposedly refers to the vibrations of C-C groups[33]. This line is less pronounced in the spectrum of DND 10 nm. Also in the IR spectrum of DND 5 nm and more so in the spectrum of DND 10 nm, there is an intensive line that can be attributed to the vibrations of the sp^3-CH group (1110-1135 cm^{-1}) and/or to the vibrations of C-O-C group (1149-1158 cm^{-1})[34].

From the analyses of the obtained IR spectra, it is following that nanodiamonds used in this work have highly oxidized but somewhat different surface with the huge number of –COOH groups.

In this work, the nanodiamond+biomacromolecule complexes were created. To do this, to the initial solutions of lysozyme and DNA of various concentrations the suspensions of DNDs at appropriate ratios were added. The used concentrations of Lys and DNA in the final suspensions are presented in Table 1 when the concentration of DNDs 5 nm was 0.5 g/L, of DNDs 10 nm – 1 g/L. Nanodiamonds of these concentrations have the approximately equal surface areas – the area from which their fluorescence originates as well the area that interacts with the environment. pH of all samples was made to be 7. In the previous paper[10], we found that used DNA bonds to the DNDs in such a way that to the one nanoparticle there is no more than one DNA chain. In the present paper, the range of DNA concentrations only at 7th point go slightly beyond this point. Concentrations of lysozyme were chosen from similar considerations: as a result of bonding of Lys to DNDs, to the one nanoparticle there is less than one Lys molecule in samples 1 to 4 and more than one but less than two in samples 5 and 6 (Table 1). All samples prior to any measurement were shacked in the vortex for 2 minutes and then left for 2 hours. All residuals were washed by a bidistilled water of the biomacromolecules that had not bonded to the DNDs surface.

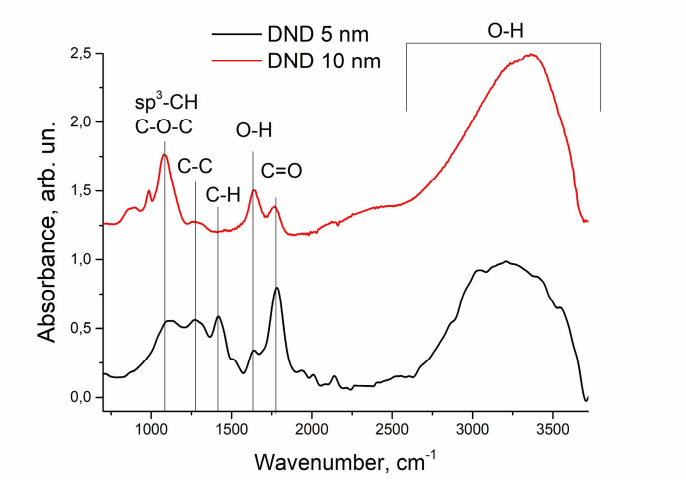

Figure 1. IR absorbance spectra of DND 5 nm and DND 10 nm.

Table 1. Studied concentrations of Lys and DND

№	Lysozyme concentration, 10^{-2} g/L	DNA concentration, g/L
1	0.1	0.5
2	0.5	1
3	1	1.5
4	4	2
5	8	2.5
6	10	3
7	-	3.5

Verification of the creation of complexes of biomacromolecules with DNDs was conducted by the following method:

1. By the absorption spectra in the case of lysozyme and Raman spectra in the case of DNA (not shown) the concentrations of Lys and DNA in supernatants were measured upon their interactions with DNDs and sedimentation of complexes. It was found that concentrations of Lys and DNA in supernatants significantly lower than that in initial suspensions. In more detail, in used range of concentrations of lysozyme almost all molecules of Lys (99%) became adsorbed on the surface of DNDs; with the surface of DND 10 nm 34% of the molecules of DNA became bonded, with the surface of DND 5 nm – 38%.

2. The IR absorbance spectra of initial substances and their complexes were obtained (Figure 2). The main characteristic bands of Lys are located at a 1500-1700 cm^{-1} range. In the 1600-1700 cm^{-1} range the lines of stretching vibrations of amide C=O and C-N (Amide I) are located, in the 1510-1580 cm^{-1} there is the line of stretching vibrations of C-N and deformation vibrations of N-H (Amide II). From the comparative analysis of IR absorbance spectra of initial substances and their complexes, it results that in the spectra of residuals of complexes all bands correspond to the bands of DNDs (bands of carboxylic –COOH groups) or to the characteristic amide bands of Lys. It means that there is no any new lines that can be attributed to the formation of new molecular groups between Lys and DND. It means that the molecules of lysozyme and nanodiamonds interact by means of physical adsorption.

A similar situation was observed with the complexes of DNDs with DNA – they bond by the physical adsorption.

In this way, we created the complexes of DND+Lys and DND+DNA in water. Furthermore, it was shown that such complexes are formed in the results of physical adsorption between DNDs and biomacromolecules.

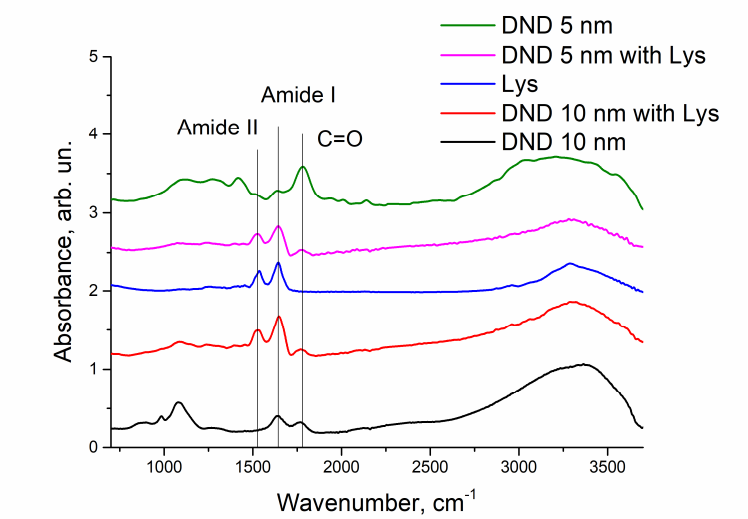

Figure 2. IR absorbance spectra of Lys, initial DNDs 5 nm and DNDs 10 nm and in complexes with Lys.

4.3 Fluorescence

In this work, the influence of interactions of lysozyme and DNA molecules with DNDs 5 nm and DNDs 10 nm in a water on fluorescent properties of DNDs was studied. For this, the fluorescence spectra of water suspensions of initial nanodiamonds, lysozyme, DNA and DND+Lys, DND+DNA complexes were obtained. Fluorescence spectra of water suspensions of DNDs, DNA, and lysozyme are presented in Figure 3. At figure 3a one can see a blue point added from the data presented in [10]. As can be seen from the figures, the emission spectrum of water suspension of DNDs is composed of the band of stretching vibrations of water with the maximum around 485 nm and of the wide band of nanodiamonds' fluorescence in the 405-830 nm range. All spectra of the fluorescence of nanodiamonds were normalized on the area of the band of stretching vibrations of water. As can be seen from the given spectra, DNA and Lys do not fluoresce when excited by radiation with a wavelength of 405 nm.

From obtained results, it is following that fluorescent properties of DNDs changes in result of interactions between nanodiamonds and biomacromolecules.

The parameter F_0 was used for quantitative estimation of the DNDs fluorescence[36]. F_0 is equal to the integral intensity of the fluorescence to the integral intensity of water stretching band (Figure 4). The parameter F_0 for the DNDs suspension without any biomacromolecules would be named F_0^I, for DNDs 5 nm F_0^I=6.10±0.04 arb. un. and for DNDs 10 nm F_0^I=3.57±0.03 arb. un. Such a difference in an integral intensity of fluorescence for DNDs 5 nm and DNDs 10 nm in case of equal surface areas in suspensions is probably caused by different amounts of surface fluorophores, which are associated with different amounts of oxygen-containing groups[22] (Figure 1) and with the presence of a certain amount of sp^2-hybridized carbon on the surface of the DNDs 5 nm[31].

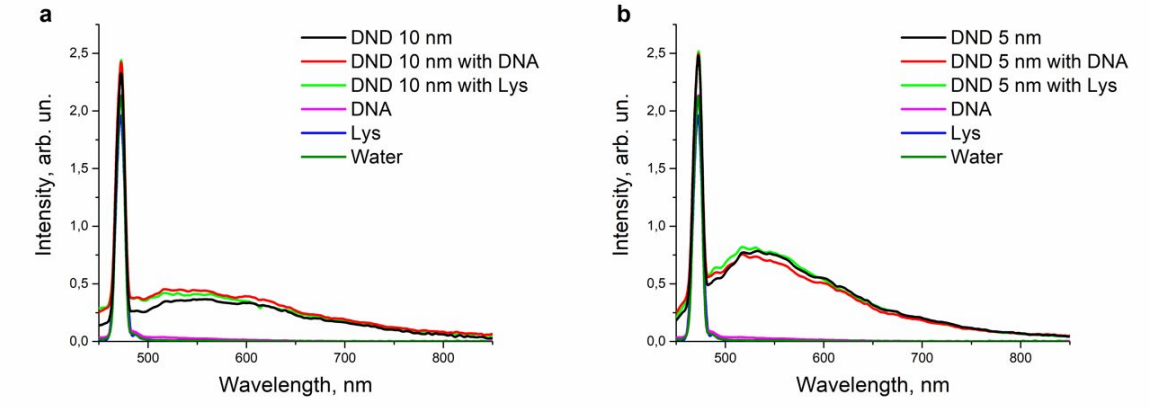

Figure 3. Fluorescence spectra of water suspensions of DND 10 nm in water and in complexes with DNA and with Lysozyme, water, DNA and lysozyme in water (a) water suspensions of DND 5 nm in water and in complexes with DNA and with Lysozyme, water, DNA and lysozyme in water (b). The concentration of DNA was 2.5 g/L, of Lys – 0.08 g/L, DNDs 5 nm – 0.5 g/L, DNDs 10 nm – 1 g/L. All spectra were normalized on the area of the band of stretching vibrations of water.

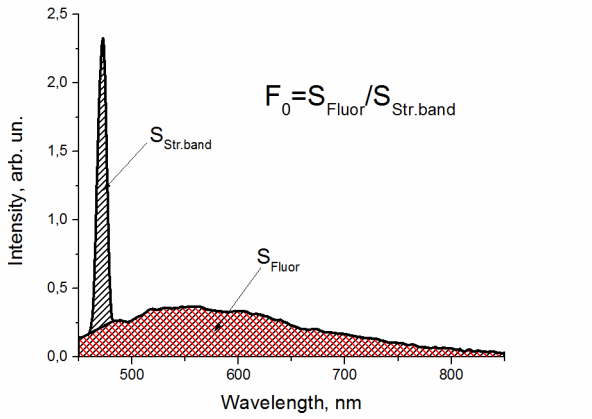

Figure 4. Illustration of the F_0 definition.

Figure 5 shows dependencies of the ratio of parameter F_0 to the F_0^I for each suspension of complexes of DNDs with biomacromolecules from the concentration of DNA (Figure 5a) or Lys (Figure 5b) in suspensions. One can see that fluorescence of both DNDs decrease in case of small concentrations of DNA (less than 1 g/L) and of Lys (less than 0.01 g/L) in water, but it increases with bigger concentrations of biomacromolecules. Furthermore, the fluorescence of DNDs 5 nm and of DNDs 10 nm changes in different ways in the result of interactions with biomacromolecules: fluorescent properties of DNDs 10 nm change faster and stronger than the ones of DNDs 5 nm (Figure 5).

The increase of DNDs fluorescence in complexes with biomacromolecules in water with the addition of interacting with DNDs surface molecules of DNA or Lys may be explained in that way: when DNDs surface is occupied by biomacromolecule, its interaction with nearest molecules of water decreases. Previous results of our group [26,27,35] showed that protic solvents, especially water, strongly quench the DNDs fluorescence. This quenching is dependent on the strength of hydrogen bonds in solvents and as a result, of hydrogen bonds between molecules of protic solvents and functional surface groups of DNDs surfaces: the weaker hydrogen bonds – the stronger fluorescence of DNDs. In the case of formation of complexes of DNDs with biomacromolecules, the influence of protic solvents decreases as the

DNDs surface area that interacts with biomacromolecules increase. The difference in the changes of fluorescent properties of DNDs 10 nm and DNDs 5 nm is likely associated with the different composition of their surface.

However, the decrease of DNDs fluorescence at a small number of adsorbed biomolecules indicates the presence of more complex processes. It is possible that macromolecules adsorbed on the surface of DNDs change the surface energy levels in a way that leads to the quenching of the fluorescence of DNDs, yet the decrease of the influence of water further overcomes this additional quenching – and the intensity of the fluorescence begins to increase. However, the further experiments are needed to fully establish and test this hypothesis.

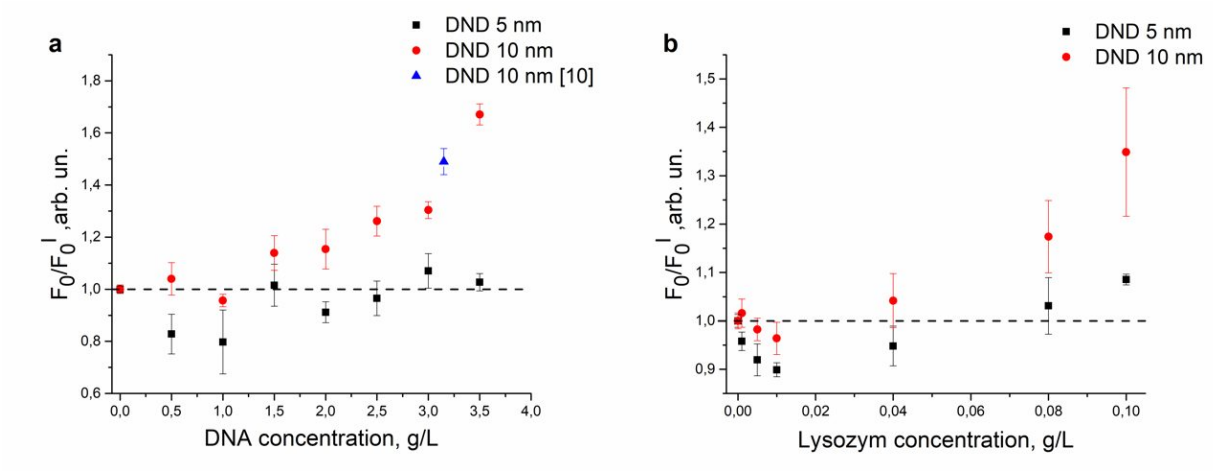

Figure 5. Dependencies of the ratio of F_0 to F_0^I for complexes with each DNDs and biomacromolecules on the DNA concentration in suspension (a) and on the Lys concentration in suspension (b).

CONCLUSIONS

In the present work, the complexes of detonation nanodiamonds of 5 nm and 10 nm sizes with the molecules of DNA and of lysozyme were created. The formation mechanism of these complexes was determined as van-der-Waals interaction (physical adsorption) between biomacromolecules and surface groups of DNDs by the FTIR absorbance method.

The change in fluorescent properties of DNDs in the result of interactions between biomacromolecules and nanodiamonds was investigated. A significant change in the fluorescent intensity of DNDs in case of interactions with both: DNA and Lys, was detected. Moreover, the change is different for DNDs 5 nm and DNDs 10 nm, which may be explained by the difference in the surface treatment and the presence of a certain amount of sp^2-hybridized carbon on the surface of the DNDs 5 nm. It was established that the fluorescent intensity of nanodiamonds increases in case of interaction with a sufficient number of biomacromolecules. The explanation is that during the formation of complexes of DNDs with biomacromolecules the influence of water decrease with the increase of the DNDs surface area that interacts with biomacromolecules. As a result, a strong quenching of DNDs fluorescence by water decreases. The problem of explanation of a nonmonotonic dependence of fluorescence intensity from biomacromolecule concentration requires a further research.

ACKNOWLEDGMENT

This study has been performed at the expense of the grant of Russian Science Foundation (project No 17-12-01481). The work of A.V. was supported by the Foundation for the advancement of theoretical physics and mathematics “BASIS”

(grant No. 17-21-2134). E.V., K.L., T.D. – samples preparation, conduction of experiment, data analysis, discussion of results; A.V. – samples characterization, discussion of results.

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