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Fluorescence of DND in suspensions

Influence of hydrogen bonds on the colloidal and fluorescent properties of detonation nanodiamonds in water, methanol and ethanol

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### **Abstract**

This paper presents the results of research of influence of hydrogen bonds with different strength on fluorescence and colloidal properties of detonation nanodiamonds with surface carboxylic groups in the solvents. It is established that the colloidal properties of detonation nanodiamonds are almost independent on hydrogen bonds strength in water, methanol and ethanol. The fluorescent properties of detonation nanodiamonds are dependent on the type of solvent: the more intensive fluorescent properties correspond to weaker hydrogen bonds in solvents.

### **Key words**

detonation nanodiamonds, hydrogen bonding, suspensions, fluorescence spectroscopy.

## 1. Introduction

The unique optical and biochemical properties of detonation nanodiamonds (DND) such as good dispersivity and chemical stability in water, fluorescent properties and their low photobleaching, low toxicity and biocompatibility, make them an perspective class of luminescent nanomaterial for application in biomedicine [1-5]. However, the misunderstanding of the mechanisms of the fluorescence of the nanodiamonds makes the use of DND as fluorescent biomarkers very difficult. Within the frameworks of the solution of this problem one of the basic problems is study of influence of surrounding molecules on optical properties of nanodiamonds.

Substantial influence of the interactions of nanoparticles with solvent molecules on the properties both of nanoparticles and solvent was demonstrated in the studies [6-17]. The authors of [6,7] have showed theoretically that the properties of nanoparticles suspensions can drastically differ from the properties of solutions of known inorganic or organic compounds. It was established that dispersed DND also significantly change the structure of solvents. According to the results of the authors [8-10] the water surrounding the surface of nanodiamonds, has specific properties that are quite different from the surrounding “bulk” water. Recently the nonlinear optical properties of water suspensions of detonation nanodiamonds, namely, their saturable absorption over a wide range of nanoparticle concentrations were discovered [11]. As a result of measurement of the dependence of pH and oxygen concentration on the ND concentration in water suspension the authors [12] have demonstrated that there is the regular exchange of electrons between the surface hydrogen of diamonds with a size range of 0.5 to 1.0  $\mu\text{m}$  and water molecules. The conclusion about electron transfer from the surface of dispersed ND in the

surrounding water was made also in the paper [13] concerning the study of DND water suspensions using X-ray photoelectron spectroscopy. This electronic exchange influences on such properties of the suspension as wettability of nanodiamond surface and Zeta potential. It is supposed that discovered electronic transitions also can influence on optical, chemical and catalytic properties of DND in water.

Using the methods of Raman spectroscopy and IR absorption in the articles [14-17] it was found that in water suspension DNDs break the structure of the surrounding water by changing the strength of hydrogen bonds in it. Moreover, the change in energy of hydrogen bonds depends on the type of DND surface functional groups [14,15]. It was found that DND with carboxyl groups on their surface weaken the hydrogen bonds more intensively in comparison with polyfunctional, fluorinated or hydroxylated nanoparticles [15]. By means of methods of vibrational spectroscopy (Infrared and Raman) and X-ray Absorption Spectroscopy the authors of [14] have performed the comparative analysis of interactions between water molecules and DND, which were functionalized by hydrophilic and hydrophobic groups. It was established that ND with hydrophobic surface groups -- hydrogenated ND -- weakens the network of hydrogen bonds in water stronger than that with the hydrophilic surface groups. Substantial influence of DND on connectivity of surrounding molecules is typical not only for water suspensions but also for the other protonic solvents [16,17]. In its turn, the change of hydrogen bonds strength causes the change of DND properties, in particular, the optical properties [15-17]. According to the results obtained by the authors of this study earlier [15-17], the weaker are hydrogen bonds with water molecules the more intense is DND fluorescence.

Obviously, for application of DND in biomedicine as fluorescence biomarkers it is necessary to study the influence of the interactions of NDs with surrounding molecules, firstly, on optical and colloidal properties of DND. In this study the influence of solvents with different strength of hydrogen bonds on the colloidal and fluorescence properties of DND was studied using the methods of dynamic light scattering (DLS) and fluorescence spectroscopy.

## **2. Experimental part**

### ***2.1. Materials***

The suspensions of detonation nanodiamonds modified with carboxyl groups (DND-COOH) in water, ethanol and methanol were investigated.

The initial DND were synthesized by detonation of a mixture of trinitrotoluene (TNT) and 1,3,5- trinitrotoluene-1,3,5-x-triazine (RDX) in media with water cooling (“New Technologies”, Chelyabinsk, Russia). The further purification from soot and treatment of DND were performed at Adámas (Raleigh, North Carolina, USA). These procedures were described in details in [18]. The modification of purified DND by COOH groups was carried out by means of treatment of DND in air at 420°C during one hour. Primary characterization of obtained sample was performed at the International Technological Center [18,19].

To prepare the DND-COOH suspensions the bidistilled deionized water with an electrical conductivity of 0.1  $\mu\text{Sm/cm}$  and alcohols containing 96% and 99.9% of ethanol and methanol, accordingly, (Sigma Aldrich) were used. Only analytical grade chemicals were used. The water and alcohol suspensions of DND-COOH (hereinafter -- DND) were prepared in concentration range from 0 up to 1.8 g/L of DND with the increment 0.1 g/L. The DNDs suspensions were treated 180 min in ultrasonic bath (Bandelin Sonorex RK-31).

This choice of solvents was due to their substantially different polarity, and, consequently, the volume average “effective” strength of hydrogen bonds. As the “effective” strength of hydrogen bond it should be understood the energy of all hydrogen bonds per hydrogen bond in a given volume of solution. In other words, it is the force acting on a nanoparticle in suspension from the averaged single hydrogen bond in the volume. According to [20,21], selected solvents to form the following series in descending order of polarity (hence, descending the average “effective power” of hydrogen bonds): water > methanol > ethanol.

## ***2.2. Experimental setup***

The study of DNA suspensions was carried out using spectroscopy IR absorption, dynamic light scattering and fluorescence spectroscopy.

Spectra of IR absorption were obtained using Varian 640-IR FTIR spectrometer (Resolution  $4\text{ cm}^{-1}$ , ATR attachment with the ZnSe crystal).

Colloidal properties of DNA 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). For the numerical processing of the obtained correlation functions the software package CONTIN was used.

Fluorescence spectra of DND suspensions were measured using the laser spectrometer. Excitation of the fluorescent signal of DND suspensions was performed by blue diode laser (wavelength 405 nm, power 50 mW). Integral spectra were measured in  $90^\circ$  geometry with the help of a monochromator (Acton 2500i, focal length 500 mm, grade 1800 grooves/mm) and PMT (Hamamatsu H8259-01). The width of the entrance and exit slits was  $500\ \mu\text{m}$  (it provided a resolution 0.5 nm). Spectra were measured in the region 410–750 nm. A thermostabilizing

system allowed setting up and controlling the temperature of the sample with an accuracy of 0.1°C.

### 3. Results and discussion

#### 3.1. Spectroscopy of IR absorption

To control the stability of the functional cover of DND-COOH in the suspensions the IR absorption spectra were obtained for the DND-COOH samples that were dried from the water, methanol and ethanol solvents (Fig.1). One can see from Fig.1 that on the surface of all samples the carboxyl groups dominate: in the region of 1050-1100  $\text{cm}^{-1}$  and 1350-1500  $\text{cm}^{-1}$  there are vibrational bands of CO groups, in the region 3000-3900  $\text{cm}^{-1}$  there are vibrational bands of OH groups.

#### 3.2. Colloidal properties of DND in water and alcohol suspensions

Using DLS method the sizes of DND particles were measured in suspensions with different solvents -- in water, methanol and ethanol. The obtained distributions of aggregate sizes are shown in Fig. 2.

The sizes of DND in water were (10±1) nm. As it follows from the obtained data, in alcohol suspensions the sizes of the main part of DND did not undergo significant changes. In ethanol and methanol suspensions the sizes of DND were (11±1) nm. When DNDs are suspended in the alcohol a small part of DND (8% in methanol, 13% in ethanol) aggregated into particles with a size of 36 nm. Thus, the «effective» strength of hydrogen bonds has no significant impact on the colloidal properties of DND in the studied solvents.

#### 3.3. Fluorescent properties of DND in water, methanol and ethanol

The fluorescence spectra of DND suspensions in water, methanol and ethanol were obtained in the range of DND concentration range from 0 up to 1.8 g/L of DND with the increment 0.1 g/L. In Fig.3 one can see the Raman and fluorescence spectra of DND suspension with concentration 1.8 g/L in all three solvents. The broad band ranging from 500 to 700 nm with maximum near 580 nm is the fluorescence spectra of DND-COOH. The bands in the range from 560 to 575 nm are caused by stretching vibrations of CH groups of alcohols, and the broad band with maximum near 580 nm is caused by stretching vibrations of OH-groups of water and alcohols.

In Fig.4 and Fig.5 one can see the Raman and fluorescence spectra of DND in water and methanol suspensions with different DND concentration, accordingly. As it can be seen from the obtained data, the DND fluorescence intensity monotonously increases with increases of the DND concentration. The parameter  $F_0 = S_{FL}/S_R$  ( $S_{FL}$  is the integral intensity of DND fluorescence,  $S_R$  is the integral intensity of Raman stretching band of OH-groups of water (Fig.4) or the integral intensity of Raman stretching bands of CH and OH groups of alcohol (Fig.5)) was used for a quantitative characterization of the fluorescent bands.

For all obtained spectra the parameters  $F_0$  were calculated and the dependences of the parameter  $F_0$  on the DND concentration in water, methanol and ethanol were obtained (Fig.6). As it is seen from the obtained results, at the same concentration of nanoparticles the DND fluorescence is most intensive in ethanol and less intensive in water. Thus, the intensity of DND fluorescence in the solvents depends essentially on the «effective» strength of hydrogen bonds in suspensions: weaker hydrogen bonds in the surroundings of DND correspond to more intensive fluorescence of nanoparticles. These conclusions are in good agreement with the results obtained



by us earlier for nanodiamonds with different surface functionalization in water: the weaker hydrogen bonds between the surface functional groups of DND and surrounding water molecules correspond to the stronger fluorescence of DND [14,15].

The significant dependence of the DND fluorescent properties on the «effective» strength of hydrogen bonds with the surrounding solvent molecules again confirms the hypothesis about the surface mechanisms of DND fluorescence [22]. The electrostatic nature of hydrogen bonds allows supposing that the change in the fluorescent properties of DND in the solvents containing hydrogen bonds occurs as the result of changes in the surface electron-excited states of DND due to charge transfer. Surface groups, such as C-O, C = O and O = C-OH, can introduce trapping surface states with different energy levels. As a result of formation of hydrogen bonds with the surrounding molecules the energy levels of these states change. In water a uniform homogeneous network of strong hydrogen bonds is formed around DND. In methanol and ethanol, the number of hydrogen bonds per unit volume is smaller than that in water, so the “effective” strength of hydrogen bonds is much smaller. The network of hydrogen bonds which is formed by the alcohols molecules with the surface functional groups of DND, is sparse and inhomogeneous (Fig.7). As a result, the charge transfer between the surface of DND and water molecules is much more active than that in methanol and especially ethanol. That is why the fluorescence of DND at the same DND concentrations correlates with the «effective» strength of hydrogen bonds in the solvents, namely, it increases with weakening of hydrogen bonds according to the following row: water, methanol, ethanol.

## 4. Conclusions.

In this study the colloidal and fluorescence properties of DND-COOH in solvents with different polarity (with different «effective» strength of hydrogen bonds) -- water, methanol, ethanol - were studied.

It has been established that the strength of hydrogen bonds in the surrounding of DND in the studied solvents has practically no effect on the colloidal properties of DND-COOH.

The significant dependence of the DND-COOH fluorescent properties on the strength of hydrogen bonds in suspensions was established. Weaker hydrogen bonds in the surrounding of DND correspond to more intense fluorescence of nanoparticles.

The authors explain the revealed effects with different degree of change in populations of the upper excited levels of surface groups of nanoparticles under the influence of hydrogen bonding: uniform network of strong hydrogen bonds of water induces stronger depletion of the population of upper excited levels of surface traps than non-regular networks of weaker hydrogen bonds of methanol and ethanol. This finding could be important in study of the still unexplained mechanisms of the fluorescence of DND.

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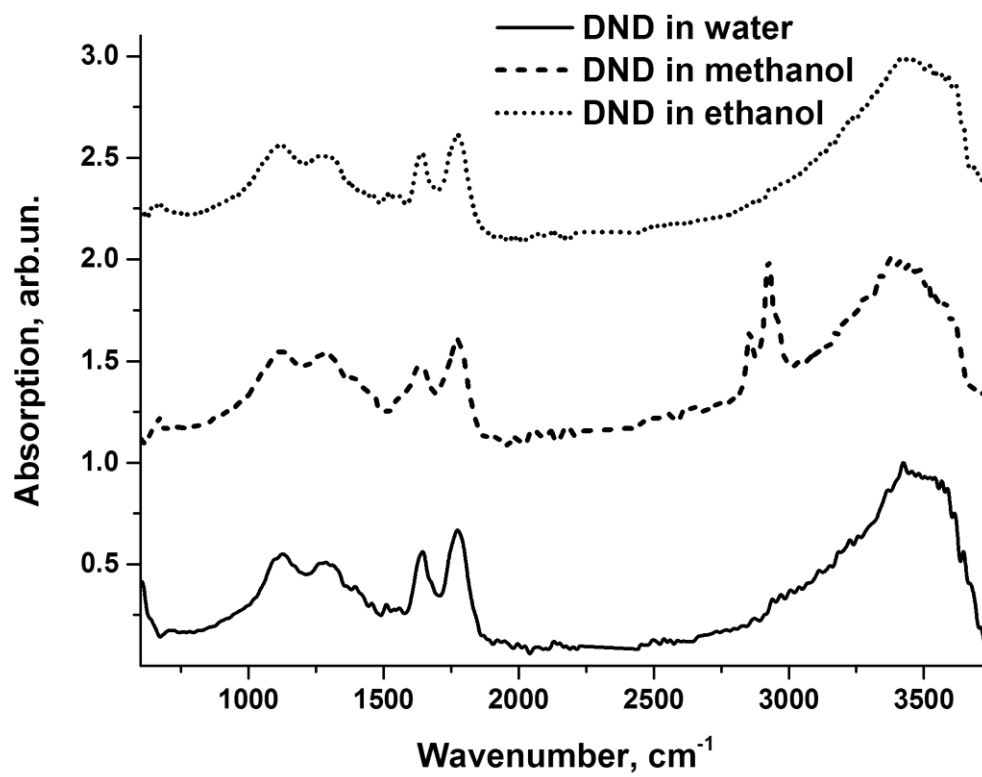


Fig.1 IR absorption spectra of DND, dried from different solvents.

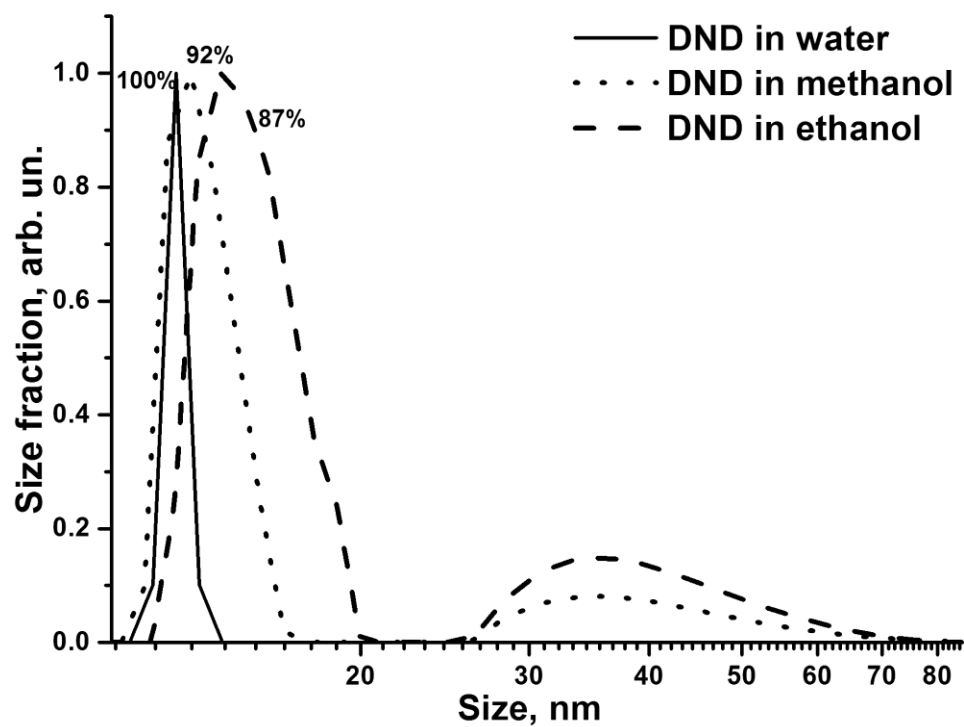


Fig.2 DLS analysis of DNDs: Particle size distribution of DNDs in suspensions with different solvents.

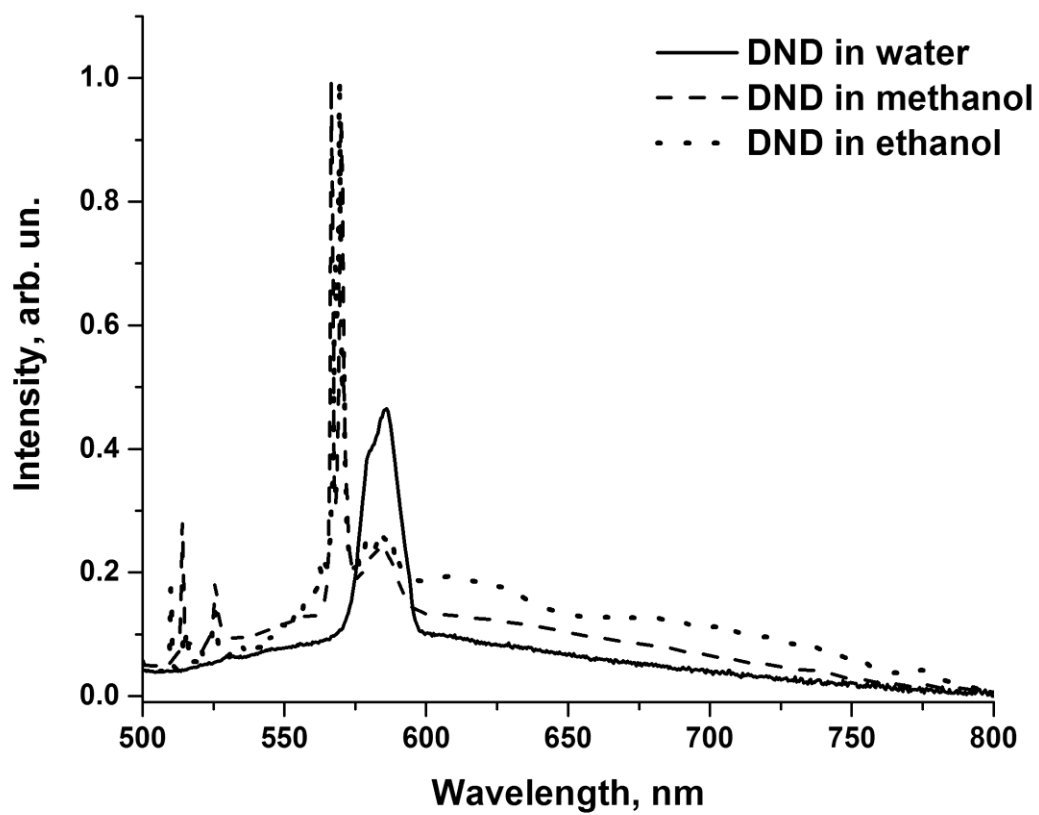


Fig.3 Fluorescence and Raman spectra of DND suspensions in water, methanol and ethanol with the same concentration 1.8 g/L.



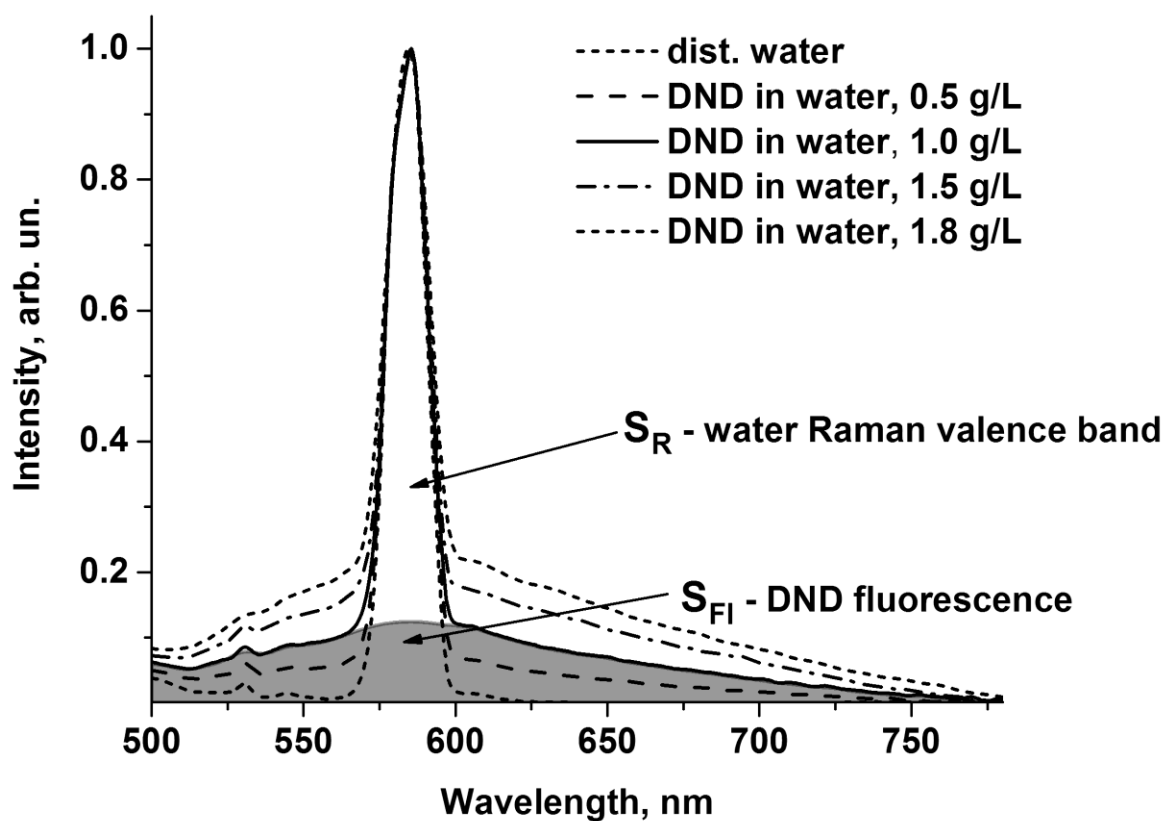


Fig.4. Raman and fluorescence spectra of DND suspensions in water with different concentrations. Spectra were normalized to the maximum of intensity.

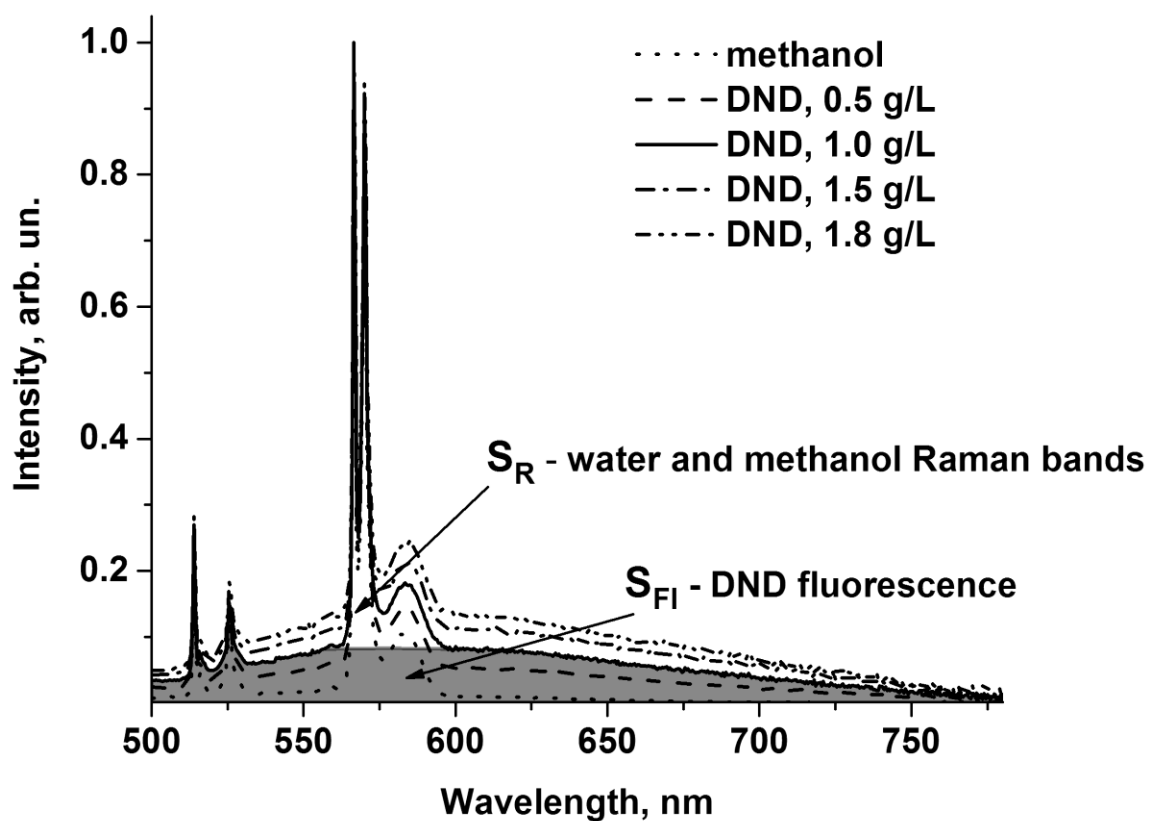


Fig.5. Raman and fluorescence spectra of DND suspensions in methanol with different concentrations. Spectra were normalized to the maximum of intensity

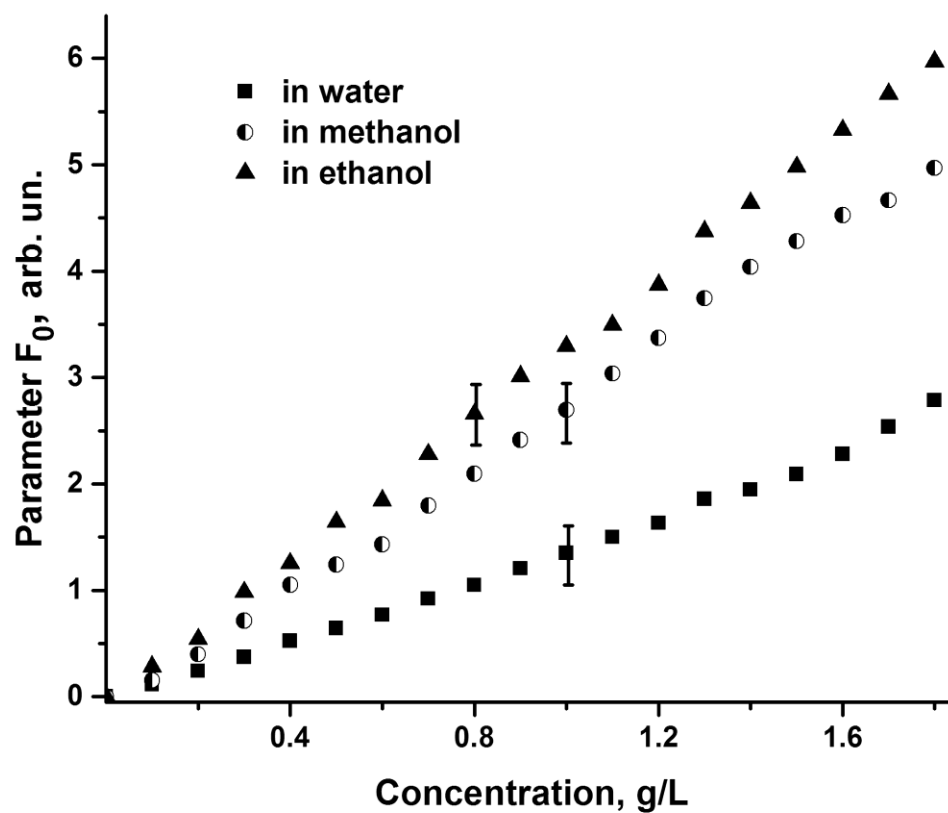


Fig.6. Dependencies of the fluorescence parameter  $F_0$  on the DND concentration in water, methanol and ethanol.

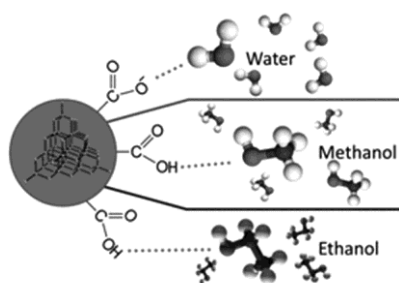


Fig.7. Hydrogen bonds between the surface functional groups of DND and the solvent molecules.