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Effect of nanodiamonds on fluorescence enhancement of tryptophan phototransformation reaction products in the presence of halocarbons

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The role of nanodiamonds in the reaction of photochemical transformation of tryptophan in the presence of halogen hydrocarbons has been studied. The photochemical transformation of free tryptophan in a suspension with diamond nanoparticles and in a hybrid complex with them when exposed to UV radiation in the presence of chloroform is investigated. Data from stationary and time-resolved spectroscopic studies show the presence of non-radiative transfer of electron excitation energy between tryptophan molecules and its photodestruction products for the case of a covalent complex with a nanodiamond. It is shown that in the presence of energy transfer, an increase in the intensity of integral fluorescence occurs in the range of ~ 450 nm. Thus, a covalent tryptophan complex with a nanodiamond can serve as a fluorescent marker for the presence of chloroform in solution.

Keywords: nanoscale diamonds, hybrid complexes, tryptophan phototransformation, spectral-luminescent properties, fluorescence decay kinetics, chloroform.

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Introduction

Currently, the development of nanotechnologies leads to creation of hi-tech materials with unique properties and search for fields of their effective application [1–4]. Physical and chemical properties of nanomaterials are unique and different from their bulk analogues thanks to their ultrafine sizes, that are varying from 1 to 100 nm [5–7]. In recent years nanocarbon materials have become a promising alternative to other nanomaterials for different process applications due to their nanoscale dimensionality, surface functionalisation capability, high chemical stability, complexability [8–10]. Among the nanocarbon materials, nanopaticles of detonation nanodiamonds can be distinguished, that can be effectively modified due to the presence of developed chemistry of surface [11] and can form hybrid organic-inorganic complexes [12,13]. Properties of detonation nanodiamonds are of great interest in many fields of research [14] due to their diverse applications [15].

In this work the effect of photochemical degradation of tryptophan on photophysical properties of its covalent and coordination complexes with nanodiamond particles has been studied. Due to the presence of carboxyl group tryptophan is convenient for conjugation with diamond nanoparticles that have amine groups. It is known that ultraviolet (UV) radiation can result in photochemical destruction of aromatic amino acids, for example, tryptophan [16]. As a result of this destruction photochemical dissociation products are formed: kynurenine and its derivatives, which are non-fluorescent in the spectral region typical for amino acid. Fluorescence of tryptophan and its products essentially depends on properties of the environment [17–19]. The photochemical transformation of free tryptophan in a suspension with diamond nanoparticles and in a hybrid complex with them when exposed to UV radiation in the presence of chloroform is investigated. The presence of organohalogen compounds in aquatic environments results in the emergence of an intensive fluorescence of tryptophan phototransformation products after exposure to radiation [20]. The data of time-resolved spectroscopic investigations shows the presence of non-radiative transfer of electron excitation energy between tryptophan molecules and its photodestruction products for the case of a covalent complex with a nanodiamond.

The obtained results can be used for development of highly sensitive optical test-system of chlorinated organics indication in the environment based on the photochemical transformation of tryptophan in the presence of chloroorganic compounds.

Experimental part

Preparation of samples

For the synthesis of organo-inorganic hybrid complex of tryptophan with nanodiamonds (ND-Tr) and spectral measurements we used L-tryptophan (Tr) by „Sigma-Aldrich“ (Germany), detonation synthesis nanodiamonds (ND) by „Sinta“ NP CJSC (Minsk, The Republic of Belarus), 1, 1′-carbonyldiimidazole (CDI), dimethylaminopyridine (DMAP), and dimethylsulfoxide (DMSO) by „Sigma-Aldrich“, diethyl ether, nonaqueous pyridine,

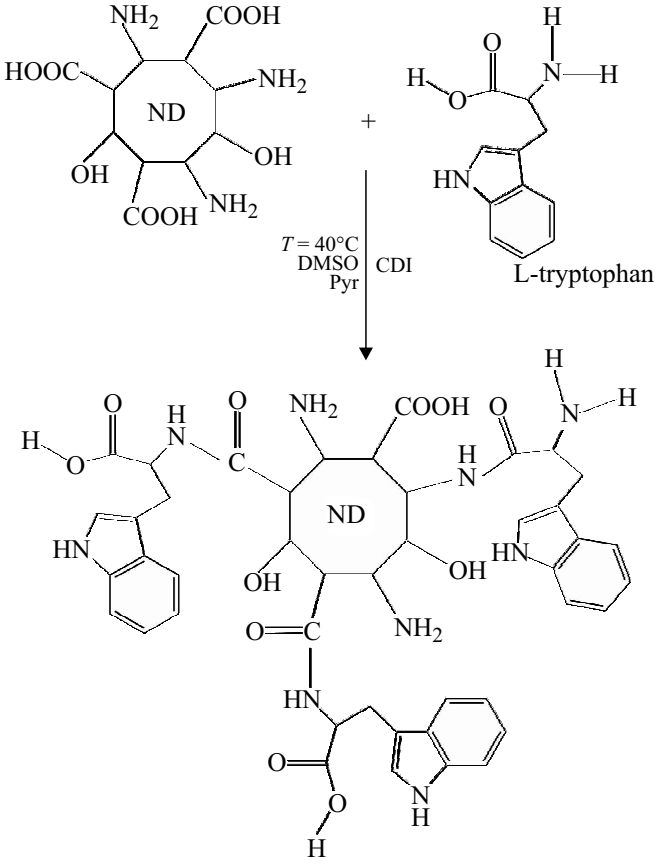

Figure 1. Scheme of ND-Tr complex synthesis.

ethyl alcohol, acetone, and glycerine of (chemically pure) reagent grade. The synthesis was performed in the atmosphere of nitrogen and in nonaqueous solvents. Nanodiamond powder (50 mg) in 50 ml of nonaqueous DMSO and 6 ml of nonaqueous pyridine (Pyr) were agitated in a magnetic agitator for 1 h and dispersed for 10 min in vortexer. The obtained colloid was treated by ultrasound (22 kHz) for 40 min, then 30 mg of 1.1′-CDI were added to the reaction flask and agitated for 3 h at 40°C. Then 50 mg of L-tryptophan and 15 mg of DMAP were introduced into the reaction flask and continued the agitation in the magnetic agitator for 48 h at a room temperature. The ND-Tr (Fig. 1) complex obtained in this way was centrifuged (for 20 min at 10000 rpm), the resulted residue was cleaned of reaction products not related to ND by washing 2 times of 10 ml of DMSO and 10 ml of ethyl alcohol with subsequent centrifugation (for 20 min at 10000 rpm). The washing solution (washing of unbound L-tryptophan) was observed under UV until visual disappearance of the blue glow.

The stable nonaqueous suspension of nanodiamonds with L-tryptophan (ND + Tr) ($C_{Tr} = 1.0 \cdot 10^{-4}$ M) was obtained in the following way: 10 mg of ND were mixed with 100 ml of dimethylsulfoxide in a 100-ml closed glass flask and agitated in a magnetic agitator for 1 h. Then the mixture was treated under ultrasonic radiation using an ultrasonic generator with a frequency of 24 kHz for 20 min. The mixture was settled for 12 h until clarification of the liquid (until a stable suspension is formed) and residue settlement. In the first fraction (transparent liquid) L-tryptophan (2 mg) was added and the mixture was agitated in a magnetic agitator for 10 min.

To record absorption spectra, as well as fluorescence spectra, fluorescence excitation and fluorescence kinetics spectra, solutions of free tryptophan in a suspension with diamond nanoparticles ND + Tr and in a hybrid complex of ND-Tr complexes in DMSO at $T = 293$ K were prepared.

Spectral measurements

Absorption spectra of Tr solutions, ND-Tr complex, and ND + Tr suspension in DMSO in the presence of chloroform ($1.0 \cdot 10^{-3}$ M) were recorded at Varian Cary 500 double-beam spectrophotometer (USA). Measurements were conducted in quartz cells with a thickness of 1 cm.

Stady-state spectra of fluorescence, spectra of fluorescence excitation were measured using Fluorolog-3 (Horiba Scientific, USA–France–Japan) multifunctional spectrofluorometer. In stationary measurements a 450 W continuous xenon lamp was used as a source of fluorescence excitation, which radiation was passed through a double monochromator to extract the required wavelength of the excitation.

All spectral measurements were conducted in the standard 90°-geometry at a room temperature. The fluorescence recording channel used iHR320 (Horiba Scientific) diffraction spectrometer and PPD-850 (Horiba Scientific) thermoelectrically cooled PMT as a detector. Fluorescence spectra and fluorescence excitation spectra were corrected for the spectral sensitivity of the instrument.

Kinetics of fluorescence decay were recorded by the method of time-correlated single photon counting. Picobrite PB-265 (Horiba Scientific) pulsed LED with maximum radiation intensity at a wavelength of 264 nm and a half-height pulse duration of 0.85 ns and Picobrite PB-340 (Horiba Scientific) pulsed semiconductor LED with maximum radiation intensity at a wavelength of 342 nm and a half-height pulse duration of 0.75 ns were used as a source of fluorescence excitation. Recording wavelength were selected using ML44 (SOLAR LS) monochromator. Fluorescence signal was detected using R3809U-50 (Hamamatsu) PMT, then it was amplified by HFAH-40 (Becker & Hickl GmbH) pre-amplifier and processed by SPC-130 (Becker & Hickl GmbH) time-correlated photon counting module.

Decay of the fluorescence signal was approximated in FAST software (Edinburgh Instruments) by two- or three- exponential dependence using the following relationship [21]:

$$I_f(t) = B + \sum_i A_i \exp(-t/\tau_i),$$

where $I_f(t)$ — fluorescence intensity as a function of time, τ_i — decay time constants, B, A_i — experimental constants.

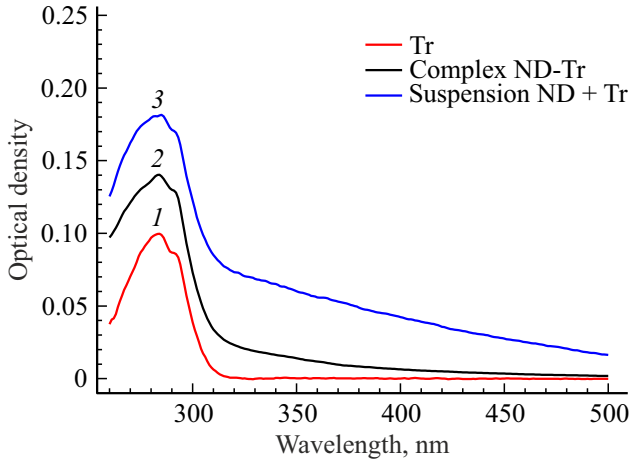

Figure 2. Absorption spectra of solutions: *1* — tryptophan ($1.0 \cdot 10^{-4}$ M), *2* — ND-Tr complex, *3* — suspension of ND + Tr ($1.0 \cdot 10^{-4}$ M) in DMSO in the presence of chloroform ($1.0 \cdot 10^{-3}$ M).

Weight contribution of the f_i component with time constant τ_i was estimated by the following equation:

$$f_i = \frac{A_i \tau_i}{\sum\limits_i A_i \tau_i}.$$

Mean lifetime of excited state for the case of recording the fluorescence decay, mean excited state lifetime τ_0 was determined as:

$$\tau_0 = \frac{\sum\limits_i A_i \tau_i^2}{\sum\limits_i A_i \tau_i}.$$

The approximation was made using the least square method, the approximation quality was estimated by the reduced parameter χ^2.

Results and discussion thereof

Fig. 2 shows absorption spectra of solutions of tryptophan, ND-Tr complex, and suspension of ND + Tr in DMSO in the presence of chloroform ($1.0 \cdot 10^{-3}$ M). In the absorption spectra of ND-Tr complex and suspension of ND + Tr there is a scattering contribution due to the presence of diamond nanoparticles in the solutions with particle size much less than the wavelength of light, which leads to a visible difference in the optical density in the maximum of absorption.

For all chloroform-containing solutions a distinctive absorption band was observed in the range of 240–310 nm with its maximum at 280 nm, which is referred to the first electronic absorption band $S_0 \rightarrow S_1$ of tryptophan. Fluorescence of solutions of tryptophan in DMSO, ND-Tr complex in DMSO, and suspension of ND + Tr in DMSO in the presence of chloroform ($1.0 \cdot 10^{-3}$ M) were investigated. When exposed to UV radiation (280 nm), a brake of pyrrole ring of indole takes place in the solution of tryptophan with formylkynurenine, kynurenine and other final tryptophan phototransformation products (TPP) formed [22], which manifest a fluorescence maximum in the range of ~ 450 nm and higher with excitation at a wavelength of 365 nm. Tryptophan solutions were exposed to radiation of a 450 W xenon lamp through a monochromator at a wavelength of 280 nm with a spectral slit-width of 14.7 nm. Radiation power density was ~ 8 mW/cm^2, radiation exposure time was 10 min.

Fig. 3 shows fluorescence spectra of solutions of tryptophan, ND-Tr complex, and suspension of ND + Tr in DMSO before and after sample exposure to radiation (excitation wavelength is 365 nm) and fluorescence excitation spectra of TPP products after exposure to radiation (recording wavelength is 450 nm). Spectral slit-width at the monochromator output was 1.5 nm.

Fig. 4 shows fluorescence spectra of solutions of tryptophan, ND-Tr complex, and suspension of ND + Tr in DMSO in the presence of chloroform ($1.0 \cdot 10^{-3}$ M) before and after sample exposure to radiation (excitation wavelength is 365 nm) and fluorescence excitation spectra of TPP products in the presence of chloroform after exposure to radiation (recording wavelength is 450 nm). Spectral slit-width at the monochromator output was 1.5 nm.

For all three chloroform-containing test-systems after exposure to radiation with the excitation at 365 nm the emergence of a wide intensive fluorescence band was observed in the spectral range from 400 to 600 nm with a maximum near 450 nm corresponding to fluorescence of tryptophan phototransformation products (formylkynurenines, kynurenines, and other final tryptophan photodegradation products). It can be seen from the analysis of fluorescence spectra in various test-systems that in the case of ND-Tr

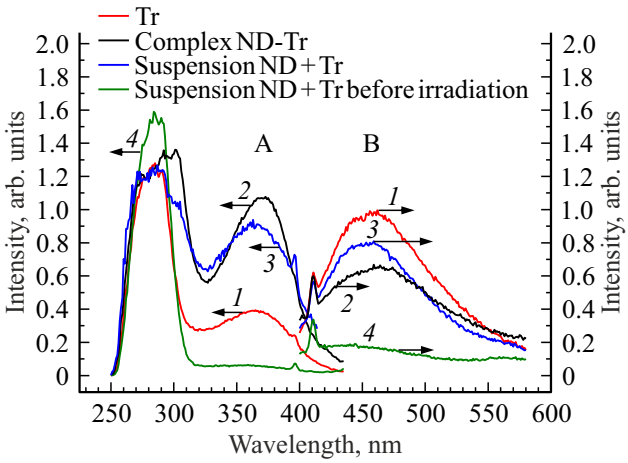

Figure 3. Fluorescence excitation spectra (A) and fluorescence spectra (B) of compounds in DMSO: *1* — tryptophan ($1.0 \cdot 10^{-4}$ M), *2* — ND-Tr complex, *3* — suspension of ND + Tr ($1.0 \cdot 10^{-4}$ M) after exposure to radiation at 280 nm, *4* — fluorescence excitation spectrum (A) and fluorescence spectrum (B) of ND + Tr suspension before exposure to radiation. Excitation wavelength is 365 nm, recording wavelength is 450 nm.

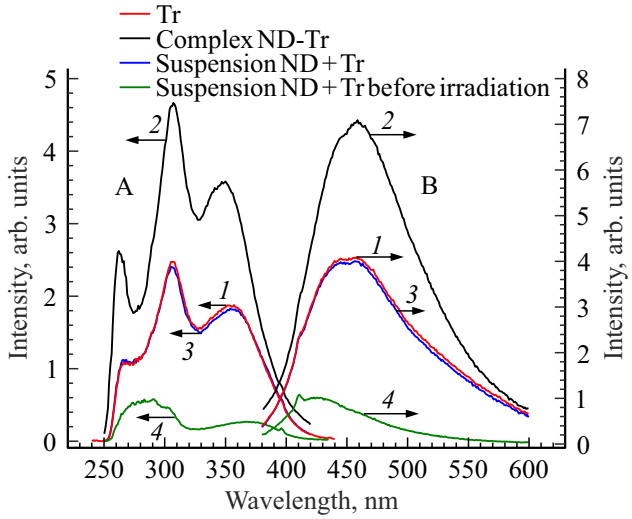

Figure 4. Fluorescence excitation spectra (A) and fluorescence spectra (B) of compounds in DMSO in the presence of chloroform ($1.0 \cdot 10^{-3}$ M): *1.0* — tryptophan ($1.0 \cdot 10^{-4}$ M), *2* — ND-Tr complex, *3* — suspension of ND + Tr ($1.0 \cdot 10^{-4}$ M) after exposure to radiation at 280 nm, *4* — fluorescence excitation spectrum (A) and fluorescence spectrum (B) of ND + Tr suspension before exposure to radiation. Excitation wavelength is 365 nm, recording wavelength is 450 nm.

complex in DMSO the fluorescence intensity of tryptophan phototransformation products is significantly higher, the reaction runs considerably faster, and the accumulation of the final product – kynurenine – is clearly manifested, as evidenced by the fluorescence spectrum *2* in Fig. 4.

It can be noted, that in all three systems two distinctive maxima are manifested in excitation spectra at wavelengths of ~ 306 and ~ 350 nm. The spectral band with a maximum at 260 nm in excitation spectra may be referred to the excitation spectrum of kynurenine, one of tryptophan phototransformation products. This assumption corresponds to the absence of the above-mentioned band in the excitation spectrum of the solution not exposed to radiation. The maximum at 306 nm corresponds to absorption of the tryptophan, which is not completely degraded after exposure to radiation. The second band in excitation spectra with a maximum near ~ 350 nm also corresponds to absorption of the kynurenine; with the excitation in this range (365 nm) its fluorescence spectrum is manifested with a maximum near ~ 450 nm. Therefore the intensive fluorescence spectrum *2* in Fig. 4 with maxima at ~ 450 nm and higher wavelengths is mainly attributable to the glow of kynurenine. The absence of clearly expressed short-wave bands of kynurenine in excitation spectra of irradiated solutions without chloroform may be related to the considerably lower efficiency of tryptophan phototransformation in this case. The presence of a rather intensive maximum near 300 nm in the excitation spectrum corresponding to the absorption of tryptophan when recording at 450 nm, where tryptophan fluorescence is insignificant, can give occasion to the assumption of photoinduced dissociation of tryptophan and formation of excited photochemical dissociation products resulted from this process, that possess long-wave fluorescence in the region of ~ 450 nm and higher wavelengths, or the excitation energy transfer from tryptophan molecules to molecules of its photochemical dissociation products.

Kinetics of fluorescence decay

Fluorescence lifetimes of tryptophan, ND-Tr complex, and suspension of ND + Tr in DMSO solution in the presence of chloroform ($1.0 \cdot 10^{-3}$ M) were measured before and after exposure to radiation for different wavelengths of excitation and recording, 350 and 450 nm. Fluorescence decay times with their relative contributions and mean lifetimes of excited state of tryptophan in three systems are presented in the table.

In the tryptophan solution not exposed to radiation, with excitation of tryptophan (264 nm) a lifetime of 7.3 ns is observed with a significant contribution of 97.1%, which corresponds to fluorescence lifetime of tryptophan ($\lambda_{reg} = 350$ nm) in DMSO [23]. In the tryptophan solution exposed to radiation, a short component of ~ 3.6 ns appears with a weight contribution of 44.3% and the component of 6.7 ns remains with a weight contribution of 47.9%, which corresponds to fluorescence lifetime of undestroyed tryptophan.

In the case of excitation of the irradiated solution of tryptophan at 264 nm, when molecules of both tryptophan and kynurenine are excited at $\lambda_{reg} = 450$ nm, emergence of a long component of ~ 17.7 ns is observed with a weight contribution of 59.8%. In the case of excitation of the irradiated solution of tryptophan at 342 nm, when only molecules of kynurenine are excited at $\lambda_{reg} = 450$ nm, the long component of kynurenine fluorescence lifetime of 15.6 ns gives a lower contribution (41%).

It's important to note, that in the case of excitation of the irradiated solution of tryptophan in the region of 264 nm, when recording the tryptophan fluorescence, its attenuation component is observed with a lifetime of 3.6 ns and a significant contribution (44.3%), which corresponds to the lifetime of excited state of kynurenine recorded at a recording wavelength of 450 nm and the same excitation directly in the absorption band of kynurenine at 342 nm. No similar behavior is observed in the solution of free tryptophan before exposure to radiation. This fact can be explained, if an assumption is made of the presence of non-radiative electronic excitation energy transfer between the excited molecule of tryptophan and molecule of kynurenine in the ground state. These molecules form a donor-acceptor pair by their spectroscopic characteristics. If in the case of excitation at 264 nm both free tryptophan and kynurenine are excited simultaneously, then, as kynurenine molecules return to the ground state, they become acceptors for the excited molecules of tryptophan, which explains the

Lifetimes of tryptophan ($1.0 \cdot 10^{-4}$ M), ND-Tr complex, and suspension of ND + Tr ($1.0 \cdot 10^{-4}$ M) in DMSO solution in the presence of chloroform ($1.0 \cdot 10^{-3}$ M) before and after exposure to radiation for different wavelengths of excitation and recording

Sample	λ_{ex}, nm	$\lambda_{reg} = 350$ nm			$\lambda_{reg} = 450$ nm		
		τ, ns; (f_i, %)	$\langle\tau\rangle$, ns	χ^2	τ, ns; (f_i, %)	$\langle\tau\rangle$, ns	χ^2
1 tryptophan	264	$\tau_1 = 1.4$ (2.9) $\tau_2 = 7.3$ (97.1)	7.1	1.09			
1 tryptophan after exposure to radiation	264	$\tau_1 = 1.2$ (7.8) $\tau_2 = 3.6$ (44.3) $\tau_3 = 6.7$ (47.9)	4.9	1.16	$\tau_1 = 1.2$ (10.1) $\tau_2 = 5.2$ (30.1) $\tau_3 = 17.7$ (59.8)	12.2	1.07
	342				$\tau_1 = 1.0$ (18.2) $\tau_2 = 3.9$ (40.7) $\tau_3 = 15.6$ (41)	8.2	1.19
2 complex ND-Tr	264	$\tau_1 = 1.7$ (5.4) $\tau_3 = 7.2$ (94.6)	6.9	1.10			
2 complex ND-Tr after exposure to radiation	264	$\tau_1 = 0.5$ (9.1) $\tau_2 = 3.2$ (20.4) $\tau_3 = 6.5$ (70.5)	5.3	1.17	$\tau_1 = 0.8$ (11.3) $\tau_2 = 3.4$ (47.6) $\tau_3 = 10.3$ (41.1)	6.0	1.25
	342				$\tau_1 = 0.7$ (13.5) $\tau_2 = 3.0$ (53.7) $\tau_3 = 9.8$ (32.8)	4.9	1.22
3 suspension ND + Tr	264	$\tau_1 = 1.5$ (2.9) $\tau_2 = 7.4$ (97.1)	7.2	1.14			
3 suspension ND + Tr	264	$\tau_1 = 2.0$ (5.1) $\tau_2 = 7.2$ (94.9)	6.9	1.23	$\tau_1 = 6.7$ (76.4) $\tau_2 = 12.1$ (23.6)	8.0	1.06
after exposure to radiation	342				$\tau_1 = 1.2$ (20.8) $\tau_2 = 3.5$ (33.5) $\tau_3 = 11.9$ (45.7)	6.9	1.17

presence of nearly the same values of the attenuation time constant in the emission of both molecules with a significant contribution and the absence of this effect for the solution not exposed to radiation. Thus, a non-radiative electronic excitation energy transfer takes place between tryptophan molecules and its photodestruction products. It is worth noting that short lifetimes of fluorescence, about 1.5 ns, that present with insignificant contribution are typical for the superfast deactivation of excited states of kynurenine and products of its secondary photochemical dissociation in DMSO [24]. The above-mentioned short decay times are observed even in solutions not exposed to radiation, which indicates the presence of tryptophan photochemical dissociation products in them in insignificant quantities.

Also, for the solution of ND-Tr complex after exposure to radiation the emergence of short fluorescence decay was observed at 264 nm excitation in case of recording in both the tryptophan fluorescence band (350 nm) and the kynurenine fluorescence band (450 nm), and with a significant weight contribution: 3.2 ns (20.4%) and 3.4 ns (47.6%), respectively. This effect could be explained by overlapping of fluorescence spectra of tryptophan and kynurenine in the region of recording with a maximum at 350 nm, however, according to [24], the fluorescence spectrum of kynurenine in DMSO with a maximum at 460 nm is beyond this region. Thus, for the case of covalent bound complex, also the presence of non-radiative energy transfer can be noted between tryptophan and its phototransformation products.

The suspension of ND + Tr at the same experiment conditions has shown another behavior. No component was observed in the attenuation of this suspension in the region of 3 ns in case of both exposed-to-radiation and unexposed-to-radiation solutions at an excitation wavelength of 264 nm. However, for the solution exposed to radiation at the excitation in the absorption band of kynurenine (342 nm) a component with a time constant of 3.5 ns and a significant contribution (33.5%) has appeared in the fluorescence of kynurenine. Thus, a conclusion can be made of the absence of electronic excitation energy transfer between tryptophan molecules and its photodestruction products in the case of suspension of ND + Tr.

The obtained results match the above-presented spectral data of fluorescence intensity of tryptophan photodestruction products. In the case of covalent bound ND-Tr complex, the presence of non-radiative energy transfer

between molecules of tryptophan and kynurenine results in a significantly amplified fluorescence signal of the solution in the emission range of tryptophan phototransformation products.

The presence of energy transfer in the covalent bound ND-Tr complex and absence of this transfer in the case of ND + Tr suspension can be explained by the fact that in the case of covalent bonding molecules of tryptophan are concentrated on the surface of nanodiamond particles. In this case the mean distance between them becomes shorter. When exposed to radiation, a part of tryptophan molecules is transformed to its phototransformation products keeping the covalent bonding. Therefore, for the non-radiative energy transfer in the case of covalent bound complex, a more favorable situation is created than that in the case of suspension.

Conclusion

The photochemical transformation of free tryptophan, tryptophan in a suspension with diamond nanoparticles and in a hybrid complex with them when exposed to UV radiation in the presence of chloroform is investigated by methods of stationary and time-resolved spectroscopy. The performed spectroscopic studies have shown that for all three chloroform-containing systems after exposure to radiation with excitation at 365 nm a wide intensive fluorescence band of tryptophan phototransformation products was observed in the range of ~ 450 nm, where in the case with ND-Tr complex in DMSO the fluorescence intensity of tryptophan phototransformation products is considerably higher and accumulation of the final product – kynurenine – is clearly manifested.

The analysis of time-resolved spectroscopic data the presence of non-radiative transfer of electron excitation energy between tryptophan molecules and its photodestruction products for the case of a covalent complex with a nanodiamond. In the case of covalent bonding the closer location of tryptophan molecules and molecules of its degradation products on the surface of nanodiamond particles promotes such energy transfer, which leads to a considerable amplification of fluorescence signal of the solution in the region of tryptophan phototransformation products emission.

The studied complexes can be used in the development of sensitive optical test-systems of chlorinated organics indication in the environment using nanodiamond particles.

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Conflict of interest

The authors declare that they have no conflict of interest.

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