FRET and NON-FRET interactions in complexes of water-soluble quantum dots and chlorin e6 molecules in different environments

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ABSTRACT

The interaction between cationic semiconductor quantum dots and chlorin e6 molecules in aqueous solutions and in polymer track membranes was investigated by spectral luminescence methods. Quantum dots and chlorin e6 molecules are found to form complexes that exhibit fluorescent resonance energy transfer (FRET) and competitive non-FRET interactions between quantum dots and chlorin e6. It was shown that FRET plays minor role in the intracomplex interactions regardless of complex formation conditions. It was also shown that FRET efficiency and photophysical properties of chlorin e6 depend on dye-to-quantum dot molar ratio (*n*).

Keywords: quantum dots, chlorin e6, FRET, track membrane.

1. INTRODUCTION

For decade photophysical properties of the complexes formed by colloidal quantum dots (QDs) and organic molecules, in particular, complexes of QD and tetrapyrrole compounds, are widely investigated (Maslov *et al* 2011). Interest in complexes based on tetrapyrrole compounds has been sparked by their ability to generate singlet oxygen ions (Warren, Smith 2008). The singlet oxygen is used in different applications such as photodynamic therapy, blood plasma sterilization, waste water treatment.

In QD/tetrapyrrole complexes efficiency of the singlet oxygen generation can be significantly increased, as compared with the free tetrapyrroles, due to an efficient photoexcitation energy transfer from QD to molecule. QDs have unique optical properties such as broad absorption spectrum with extremely high extinction coefficient, high quantum yield of fluorescence with wavelength controlled by the QD size. It is very attractive to use QDs as an energy donor in complexes with organic molecules since conditions for effective FRET can be quite easily satisfied.

For effective functioning of these complexes as the singlet oxygen generators, two

conditions should be simultaneously fulfilled: 1) tetrapyrrole molecules ability to generate singlet oxygen upon complex formation should be maintained, that can be indicated by conservation of the tetrapyrrole luminescence, and 2) the effective intracomplex photoexcitation energy transfer should occur.

In QD/tetrapyrrole complexes a formation of competitive channels of nonradiative photoexcitation energy relaxation different from FRET ("non-FRET") may take place for both donor and acceptor (Maslov et al 2011). Origin of these channels is not completely clear. Several physical mechanisms have been proposed, for example, photoinduced reversible electron transfer between QD and molecule, and formation of QD luminescence deactivation centers at the place bonding of molecule to QD.

Chlorin e6 (Ce6) is one of the tetrapyrrole compounds widely used as a photosensitizer. In some works photophysical properties of complexes between QDs and chlorin e6 are discussed. For example, possibility of efficient FRET in covalently linked QD-Ce6 conjugates in aqueous solution was demonstrated (Charron et al 2012). It was shown in this work that the luminescence of the Ce6 in complexes was strongly quenched and luminescence and absorption spectra of Ce6 differ significantly from those of free Ce6. In the same time, a conservation of the photophysical properties of the tetrapyrrole component is extremely important, since the decrease in the quantum yield of luminescence (QY) of the tetrapyrrols is usually accompanied by a decrease in efficiency of singlet oxygen generation.

In work (Valanciunaitea et al 2010) similar quenching of Ce6 luminescence with increasing the molar ratio (n) of Ce6:QD was observed. This may be caused by the decreasing the QY of the chlorin e6 as well as by decreasing efficiency of the energy transfer. Although the luminescence quenching was not estimated quantitatively, the overall picture allows suggesting formation of non-FRET competitive channels.

In this study we investigate photophysical properties of QD/Ce6 complexes with variable conditions of formation such as molar ratio of Ce6:QD, binding type, environment and size of QDs in order to understand and optimize photoinduced processes like FRET and non-FRET. Complexes were obtained in two different environments: in aqueous solution, and in poly(ethylene terephthalate) track membranes.

2. MATERIALS AND METODS

2.1 Chemicals

Bis-N-methyl-D-glucamine salt of chlorin e6 (photosensitizer Photoditazin) was purchased from VETA Grand Ltd. Photoditazin has QY=9% in aqueous solution. Trioctylphosphine oxide (TOPO), cysteamine, 2-dietilaminoetantiol (DMAET), 1-Ethyl-3-(3-Dimethylaminopropyl) carbodiimide hydrochloride (EDAC) were purchased from Aldrich. Poly-(ethylene terephthalate) (PET) membranes were obtained from FLNR JINR (Dubna, Russia).

2.2 Quantum Dot Synthesis

All semiconductor quantum dots CdSe/ZnS with different sizes cores (2.5 nm, 3.5 nm, and 5 nm) were synthesized using similar methods as previously described (Gaponik et all 2002). All QD samples have QYs >20% in hydrophobic solvents and 5-8% in aqueous solutions.

2.3 Complex formation in aqueous solutions

To form water-soluble complexes of quantum dots and Ce6 molecules two methods of QD solubilization were used. In case of covalent binding hydrophobic CdSe/ZnS/TOPO QDs with core diameter of 3.5 nm were initially solubilized by L-cysteine. In the second step L-cysteine molecules were replaced with molecules of PEG-OH and PEG-NH$_2$ with a ratio of 3 to 1. As the result of this solubilization on average one molecule of PEG-NH$_2$ per three molecules of PEG-OH on QD surface were provided. This allowed obtaining stable colloidal solutions of quantum dots. Then covalent binding of the QD surface amino group with Ce6 carboxyl functional groups using EDAC as a cross-linking reagent has been performed. Using PEG as an additional QD shell resulted in an increase in average distance between the QD and Ce6 molecules in complexes to ~ 5.5 nm.

For the complexes formed via electrostatic hydrophobic CdSe/ZnS/TOPO with a core diameter of 5.0 nm were solubilized with DMAET molecules to provide on the QD surface positive charge.

2.4 Complex formation in PET track membranes

The characteristics of PET track membranes are shown in table 1. Track membranes are produced in polymer foils using an ion track-etching technique (Apel et al 2001). Carboxyl groups are formed on the inner surface and in the loosened layer on the track pore wall. The dissociation of carboxyl groups in aqueous solutions results in the appearance of negative charges on the track pore surface (Berezkin et al 2003). This gives the opportunity to passivate the inner surface of the pores with species that can react with carboxyl groups.

Table 1. PET track membranes characteristics

Pore diameter , d	0.5 μm
Thickness , l	12 μm
Pore density, n	$2.9 \cdot 10^7$ cm^{-2}
Pore direction (relative to the foil surface), ϕ	90°

We proposed to utilize these carboxyl groups for the step-by-step formation of the water-soluble QD/Ce6 complexes in the membranes. At the first step, positively charged CdSe/ZnS/DMAET QDs with core size of 2.5 nm were embedded into the membranes due to electrostatic interaction with the carboxyl groups. Membrane with embedded QDs were impregnated with aqueous solutions of Ce6 for formation of the QDs/Ce6 complexes. In order to study Ce6 concentration dependence of the optical properties of the complex components, the samples were immersed 10 times sequentially in the Ce6 solution for 5 minutes. After each immersion the membranes

were removed from the Ce6 solutions, rinsed thoroughly by water and dried, then stationary and time-resolved optical measurements were performed.

Since Ce6 molecules have carboxyl groups, in aqueous solution these molecules are negatively charged. Our experiments have shown that the embedding Ce6 molecules into membranes without QDs does not occur due to the electrostatic repulsion of the carboxyl groups of the membrane and the Ce6. We replaced the carboxyl groups on the pore walls to amino groups with the NHS and EDAC analogously to Ref. (Niemeyer, 2004). This made possible to create the membranes with positive charges on the pore walls and embed Ce6 molecules into membranes.

2.5 Estimations of the FRET efficiency

In the Förster formalism, a distance dependence of the efficiency of FRET between donor-acceptor (D-A) pair, Q_{FRET}, is given by (Yermolaev et al 1977):

$$Q_{FRET} = \frac{R_0^6}{R_0^6 + R^6} \tag{1}$$

where R_0 (Förster radius) is the D-A distance at which the transfer efficiency is 50%, and R is the D-A distance.

R_0 can be calculated using the following equation:

$$R_0^6 = \frac{9000 \cdot \ln 10 \cdot \Phi^2 \cdot q_{0D}}{128 \cdot \pi^5 \cdot n_s^4 \cdot N} I \quad . \tag{2}$$

In this equation, Φ^2 is the orientation factor, q_{0D} is the quantum yield of the donor in the absence of quencher; N is the Avogadro number and n_s is the refractive index of the solvent. I is the overlap integral between the donor emission band and the acceptor absorption band:

$$I = \int I_D^H(\nu) \cdot \varepsilon_A(\nu) \cdot \nu^{-4} \cdot d\nu \tag{3}$$

where $I_D^H(\nu)$ is the normalized luminescence spectrum of the energy donor (QDs); $\varepsilon_A(\nu)$ is the absorption spectrum of the acceptor; ν is the wavenumber.

Formula (1) does not take into account possible appearance of additional nonradiative relaxation channels due to the complex formation. That is why we can use it only for estimation of upper limit of the FRET efficiency for donor-acceptor pair in the complexes.

The intracomplex FRET efficiency, Q_{FRET}^{Exp} can be correctly estimated from the experimental data on sensitized acceptor emission intensity (Clapp et all 2004, Zenkevich et all 2006) or the luminescence QY by using the following equation:

$$Q_{FRET}^{Exp} = \frac{\varphi_{DA}}{\varphi_A}, \tag{4}$$

where φ_{DA} and φ_A are the QY of sensitized with QDs and directly excited acceptor emission, respectively. Some difficulties here can be in direct measurement of the φ_{DA} value, because contribution of directly excited molecule emission should be correctly accounted for. It also should be noted that the use of Eq. (4) is only possible in

cases when the molecule does not change its photophysical properties upon binding with QD. Otherwise, Eq. (4) should be modified and the energy transfer efficiency can be estimated from experimental data by using formula analogous that reported in Ref (Orlova et al 2011):

$$Q_{FRET}^{EXP} = \frac{I_{AD}(\lambda'')D_A(\lambda')}{I_A(\lambda')D_{QD}(\lambda'')Q},$$

(5)

where I_{AD} is the intensity of sensitized acceptor luminescence, I_A is the intensity of acceptor luminescence directly excited by light; D_A and D_{QD} are the optical densities of the acceptor and donor at excitation wavelengths of luminescence. λ' and λ'' are the wavelengths of exciting light. The values of λ' and λ'' are usually chosen in such a way that selective excitation of PL either acceptor or donor is performed, respectively. F is the efficiency of donor luminescence quenching:

$$F = 1 - \frac{I}{I_0},$$

(6)

where I and I_0 are the donor luminescence intensities in presence and in absence of the energy acceptor, respectively.

The utilization of Eqs. (4) and (5) for estimation of the FRET efficiency is more correct than Eq. (1) because they are completely applicable in cases when the complex formation leads to appearance of the supplementary nonradiative transitions in donor (QD), and also when the acceptor luminescence quantum yield in complex is not the same as in the case of free acceptor.

2.6 UV/Vis Absorption and luminescence detection

A fluorescent spectrophotometer, Cary Eclipse (Varian), and a spectrophotometer, UV-Probe 3600 (Shimadzu), were used for steady-state luminescence and absorption spectra measurements, respectively. Wavelengths of the indirect Ce6 excitation (λ'') were chosen from spectral range of 475-500 nm, where QDs can be effectively excited while the local minimum of Ce6 absorption is. For direct excitation of Ce6, wavelengths from the spectral range of 640-660 nm (λ') were chosen since strong Q(I) band of Ce6 is located there while absorption of QDs is relatively small.

3. RESULTS AND DISCUSSION

Fig. 1 shows the luminescence/absorption spectra of QDs with diameters of 2.5 nm, 3.5 nm, and 5.0 nm used in this study as well as the luminescence/absorption spectra of Ce6. In all cases spectral overlapping of the donor PL with acceptor absorption needed for the FRET is satisfied. Evidently that FRET from Ce6 to QDs is not possible because luminescence of Ce6 is in spectral range where QDs absorption is close to zero.
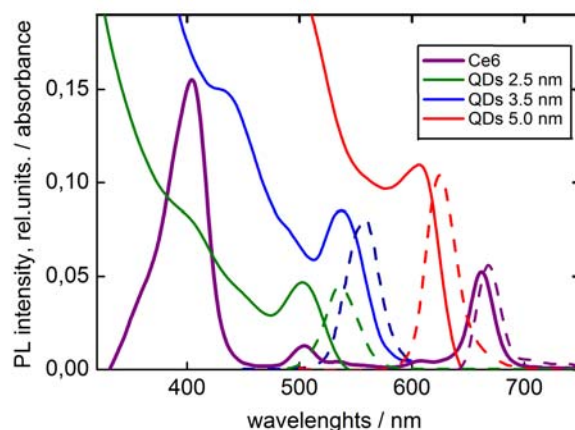
Fig. 1. The absorption (solid) and luminescence (dash) spectra of QDs of different sizes and Ce6.

In all of the complexes the quenching of QDs luminescence and sensitized luminescence of Ce6 were observed. These facts point out presence of energy transfer from QDs to molecules in the QD/Ce6 complex.

Table 2 shows calculated Forster radius, R_0 and FRET efficiency Q_{FRET} for the various QD/Ce6 pairs using Eqs. (1) – (2), the experimental values for q_{0D}, n_s =1, and $\Phi^2 = 2/3$ that is characteristic for a random orientation of dipoles both QDs and Ce6 (Clapp et al 2004, Tsay et al 2007). We suppose the distance between donor and acceptor is equal to the dot radius.

Table 2. Forster distances, R_0 and FRET efficiency Q_{FRET} for QD/Ce6 complexes with different QD sizes.

Type of bonding	Covalent bonding	Electrostatic interaction in aqueous solution	Electrostatic interaction in PET membrane
QD size, nm	3.5	5.0	2.5
Distance between donor and acceptor R, nm	55	25	17.5
Forster radius R_0, nm	46	51	47
Q_{FRET}, %	27	98	98

3.1 Covalent bonding type complexes

Fig. 2 shows the absorption spectrum of Ce6 bonded with quantum dots and the spectra of the individual components of the complexes.
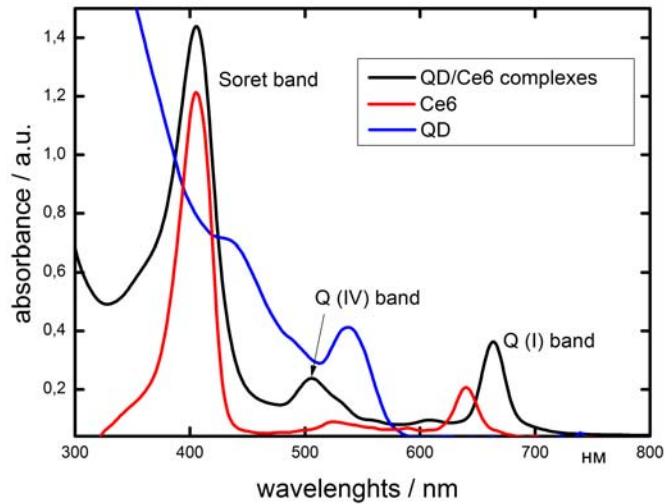
Figure 2. The absorption spectra of Ce6, QDs and QD/Ce6 in complexes in aqueous solution. The concentration of QDs: C_{QD}=4x10^{-7} mol/L, $n=C_{Ce6}/C_{QD}$ = 20.

The absorption spectrum of mixed QD/Ce6 solution is not a simple superposition of pure QDs and Ce6 absorption spectra at corresponding concentrations. Fig. 2 shows that complex formation leads to changes in the absorption spectrum of Ce6. Most pronounced changes were observed in the region of Ce6 Q(I) band, which shows a bathochromic shift to 662 nm. Also a hypsochromic shift of the Q(IV) to ~ 20 nm, and a change in the half-width of the Soret band at ~400 nm were observed. Observed absorption spectrum of chlorin e6 in complex with QDs is close to that obtained by (Charron et al 2012) as well as to absorption spectrum of Ce6 embedded into polyvinylpyrrolidone polymer chains (Isakau et all 2008). It is considered (Isakau et all 2008, Cunderlikova et al 2000), that observed modifications of the absorption spectrum of Ce6 is a typical response for changes of the molecule environment.

To evaluate the efficiency of energy transfer in the QD/Ce6 complexes using Eq. (5) their luminescence spectra excited at wavelengths of indirect and direct excitation of the Ce6 were recorded. These spectra are presented in Fig. 3. A 500 nm radiation was used for selective excitation of the QD PL within QD/Ce6 complex since at this wavelength absorption of Ce6 was negligible as compared with that of QDs. At the other hand, a 640 nm light was used for selective Ce6 PL excitation at measuring the Ce6 PL QY within the complex.

Fig. 3 shows that complete QDs PL quenching was observed as a result of complex formation.

In complexes with QDs the Ce6 PL intensity, normalized to optical density at wavelength of excitation, with excitation at wavelengths 500 nm was 1.5 times higher than with excitation at wavelengths of Ce6 direct absorption (640 nm). These facts indicate the presence of FRET.
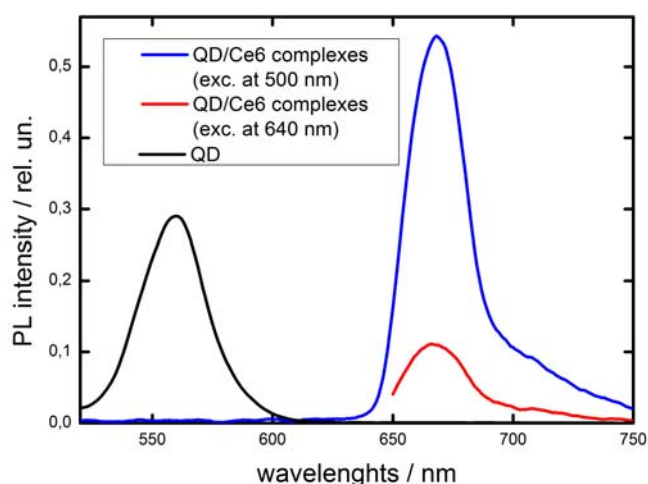
Figure 3. The luminescence spectra of QD/Ce6 complexes with excitation wavelengths at 500 nm and 640 nm and QD luminescence spectrum.

For this system, the energy transfer efficiency Q_{FRET}^{EXP}, calculated from experimental data with Eq. 5, is significantly lower than that estimated using Forster formula Q_{FRET} and shown in Table 2, and is only 8%. The relatively low value of Q_{FRET} (27%) in this case is probably caused by rather large distance between the QD and Ce6 (~ 5.5 nm) due to using modified polyethylene as the solubilizer.

Since the FRET efficiency reach only 30% of its maximum value, we can assume that QD luminescence quenching can not be explained only by FRET, which is responsible only for 30% of the QD quenching. Therefore, a presence of competitive non-FRET channels of nonradiative photoexcitation energy relaxation in QDs should be taken into account. Indirectly, it is supported by the fact that QY of Ce6 in the QD/Ce6 complexes is about 3 times lower than that in Ce6 bound with PVP reported by (Isakau et al 2008) and 2 times lower than that for Ce6 in aqueous solutions. Appearance of new channels of relaxation may be attributed to significant perturbation of the molecule under complexing with QD or the aggregation of chlorin e6 on the surface of QDs.

3.2 The electrostatic interaction in aqueous solution

QD/Ce6 complexes, formed by electrostatic interaction, were investigated for more detail analysis of the effect of number of Ce6 molecules bound with QD on energy transfer efficiency and Ce6 QY. To minimize possibility of aggregation of chlorin e6 on the surface of the QD, an average number of Ce6 molecules per one QD, $n = C_{Ce6}/C_{QD}$ molar was significantly reduced.

Complex formation as a result of the electrostatic interaction of oppositely charged QDs solubilizing molecules and functional groups of Ce6 is simply realized by mixing solutions of the components. Despite the instability of these complexes and their tendency to dissociation, they are supposed to be a good model objects to explore the dependence of the FRET efficiency and the changes in the Ce6 QY on the n. The

experiments were performed by increasing Ce6 concentration in solutions, keeping QDs concentration constant.

Absorption and luminescence spectra of Ce6 in complexes showed no significant changes in the band positions compared with previous experiment and remained unchanged upon increasing of the concentration of Ce6 in solution.

It was found that increase of the relative concentration of Ce6 in solution with QDs ($C_{QD} \sim 5 \times 10^{-7}$ mol/L) leads to quenching of the QDs luminescence and increasing the Ce6 luminescence emission (Fig. 4a).
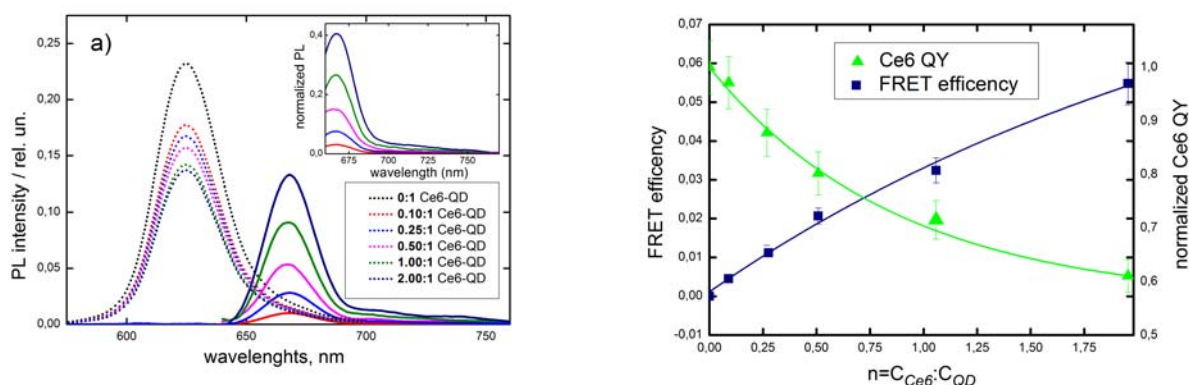

Fig. 4. (a). Evolution of the luminescence spectra of QDs (short dot) and Ce6 (solid) in the QD/Ce6 electrostatically formed complexes *vs* increasing Ce6-to-QD ratio, *n*. PL excitation at 475 nm. The intensity of Ce6 emission (dotted line) is multiplied by 2. Inset shows evolution of the PL spectra of Ce6 with excitation at 640 nm. (b) Experimental data on the FRET efficiency and Ce6 QY *vs n*.

In complexes with QDs the Ce6 PL intensity, normalized to optical density at wavelength of excitation, with excitation at wavelengths 475 nm was 5 times higher than with excitation at wavelengths of Ce6 direct absorption (640 nm). These facts indicate the presence of FRET.

Efficiency of the energy transfer, calculated using Eq. (5) and experimental values of the QYs, does not exceed 6% for *n* range. It is significantly lower than theoretical value of 98%, and indicates presence of channels of the energy relaxation different from FRET. Figure 4(b) shows that FRET efficiency increases with *n*. At the same time, QY of Ce6 bound with QDs rapidly decreases with increasing *n,* as it is shown in Fig. 4b. Origin of these dependencies is not quite clear. Indeed, when molar ratio *n* varied from 1:0.1 to 1:1, the average number of Ce6 molecules per QD was less than one. But number of Ce6 molecules per QD remains does not 1:1. This decreasing in Ce6 QY cannot be explain by interaction between close Ce6 molecules located on QD surface because number of molecules per QD remain 1:1 with *n* increasing. It was also shown that FRET efficiency and Ce6 QY have reverse concentration dependence of *n* even when *n* ≤ 1. So mechanism of the dependence of the FRET efficiency and QY of Ce6 on *n* requires additional investigations. In the first approach, we expected that this dependence may be caused by QDs aggregation in aqueous solution. To prevent it complexes in PET membranes were performed.

3.3 The electrostatic interaction in PET membrane

Aggregation of the complex components in aqueous solution is one of the possible causes of nonradiative relaxation of the excited state of the donor or acceptor.

The embedding of cationic quantum dots to pore wall layer and then adsorbing them with chlorin e6 molecules allows to prevent spontaneous aggregation of QDs and Ce6.

It was found that a gradual increase of n leads to complete quenching of QD luminescence and fatal decreasing of the luminescence intensity of Ce6 molecules, bound in the complex with QDs (Fig. 5a).

Calculation of the energy transfer efficiency indicates that FRET contribution to the intracomplex interactions do not exceed 8%.

QD/Ce6 complexes embedded to PET membrane demonstrate the same dependencies of FRET efficiency and QY of Ce6 on n as it was in case of these complexes in aqueous solution. Thus, when n increases the FRET efficiency increases while Ce6 QY decrease (Fig. 5b). It should be noted that for n=1.2 Ce6 QY fell almost to zero.
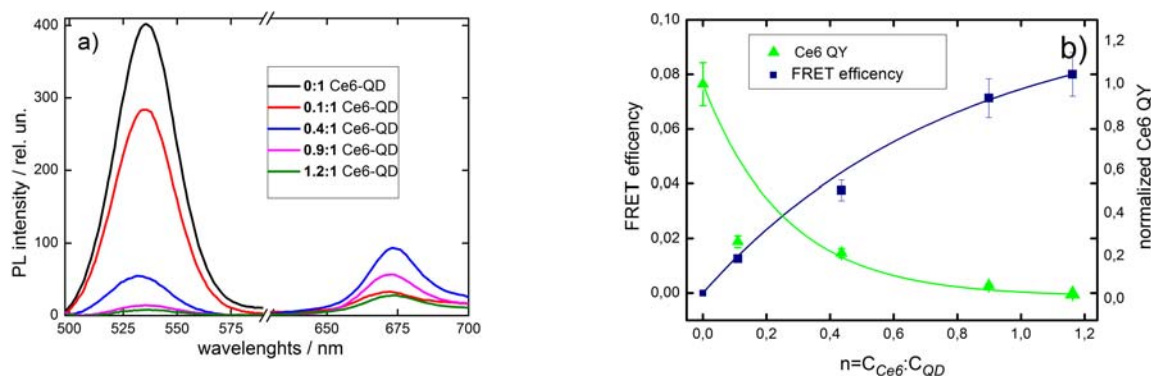

Figure 5. (a) Evolution of the luminescence spectra of QDs and Ce6 in the QD/Ce6 electrostatically formed complexes in PET membrane *vs* increasing Ce6-to-QD ratio, *n*. PL excitation at 475 nm. (b) Experimental data on the FRET efficiency and Ce6 QY *vs n*.

Summarizing experimental data, we can assume that origin dependence of FRET efficiency and QY of Ce6 on n in QD/Ce6 complexes is irrelevant with aggregation of QDs and Ce6.

We may suggest that in mixture solution complicated triple interactions occurs between the 1) solubilizer molecules (SM) located on the QDs, 2) free solubilizer molecules remaining in solution after solubilization process, and 3) chlorin e6. At low n values, the ratio between constants of complex formation of SM located on QD surface/Ce6 and free MS in solution/Ce6 is constant due to chemical equilibrium conditions. With increasing of the concentration of Ce6 in the mixture, equilibrium is shifted to complexes formation on the QD surface. If we assume that decreasing Ce6 QY occurs only as a result of interaction between QDs and molecules, then this model can explain different dependencies of the FRET efficiency and Ce6 QY on n in a range of such small n values. In any case, further investigations should be provided.

Experimental data demonstrates that non-FRET channels of nonradiative photoexcitation energy relaxation occurs in all types of QD/Ce6 and their contribution to

intracomplex energy transfer varies from 70% in covalently bonded complexes to ~ 90% in complexes formed by electrostatic interaction and may be responsible for QD and Ce6 luminescence quenching simultaneously.

Electron transfer is one of possible mechanisms of the QD luminescence quenching in the QD complexes with organic molecules. The main requirement to the quencher molecule in this case is that either both LUMO and HOMO or one of these orbitals should be located energetically within the energy gap of the CdSe core of QD. The quenching process can be considered as follows. Either an excited QD electron tunnels from the core through the shell and localizes at the LUMO of the quenching molecule or the hole, formed in the QD core because of photoexcitation, tunnels through the ZnS shell and localizes at the HOMO of the molecule. Subsequent radiationless recombination is caused by tunneling of the hole or electron the other way through the same barrier.

Mechanisms of the tetrapyrrol component luminescence quenching under complexing with QDs have not been studied in details. In reference (Orlova et al 2008) an assumption has been made that this quenching could be caused by an electron transfer between the molecule and QD.

Almost all of tetrapyrrole compounds have pronounced donor-acceptor properties. In Fig. (6) schematic representations of the relative position of the energy levels of QDs and Ce6 are shown.
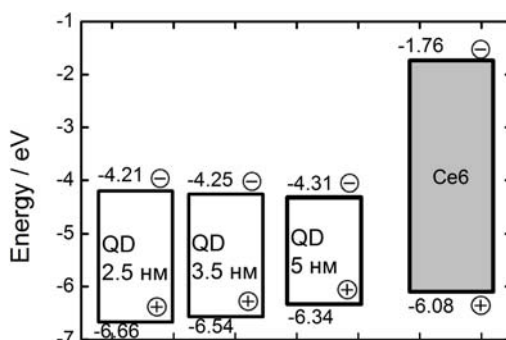

Figure 6. Energy levels diagram of QDs and Ce6 (Wang et al 2012, Sander et al 2008, Lee et al 2009).

Analysis of the relative positions of the energy levels of QDs and chlorin e6, presented in Fig. (6), shows that in complexes with CdSe/ZnS quantum dots photoinduced electron transfer from Ce6 to the QDs conduction band is possible.

In contrast to FRET, electron transfer this is a short-range process, because its efficiency drops exponentially with the electron donor to acceptor distance. In a case of the covalently-linked complexes A-D distance is large for effective electron transfer. In agreement with this is observation that FRET contribution to the intracomplex interactions in this type of complexes is much higher whereby in complexes with electrostatic interaction (30% and 5% respectively). But at the same time we can assume that electron transfer is not the exclusive non-FRET channel in QD/Ce6 complexes, because in covalently-linked complexes where electron transfer is excluded, another non-FRET channels occur.

3. CONCLUSIONS

In this study photophysical and optical properties of complexes of cationic QD and Ce6 molecules were investigated. In all systems FRET was observed. Estimated values of FRET efficiencies were relatively low, also complex formation led to significant decrease in Ce6 QY. These indicate probable formation of non-FRET channels of nonradiative photoexcitation energy relaxation of the donor and/or the acceptor. It was shown that non-FRET interactions have substantial contribution to intracomplex energy transfer. It was also shown that FRET efficiency and Ce6 QY have reverse concentration dependence of n even when $n \leq 1$.

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