Spectroscopic study of non-covalent complex formation between different porphyrin analogues and quantum dots with lipid-based coating

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In this work, we present a steady-state spectroscopic study on the formation of a non-covalent complex between commercially available CdSe / ZnS quantum dots (QD) and different porphyrin-type anionic photosensitizers. The QD surface was coated with lipid-based molecules containing terminal carboxyl groups. Porphyrins with an amphiphilic structure, such as chlorin e$_6$, carboxyphenyl and sulphonatophenyl porphyrins with one polar group, were found to form a stable complex with QD with the ability of energy transfer from QD to bound porphyrin molecules. The efficiency of energy transfer from QD to amphiphilic porphyrins was 11–14%. Upon binding to QD, a slightly more efficient energy transfer and well expressed spectral changes were observed for carboxyl- (Ce6, TC1PP) than for sulphonate-porphyrins (TS1PP). In the presence of QD, no significant spectral changes and only a negligible energy transfer (1–2%) were obtained for porphyrins with four polar groups. Based on our findings, we suggest that the formation of a QD-porphyrin complex occurs due to the hydrophobic interaction between the non-polar moiety of amphiphilic porphyrins and the hydrophobic part of the lipid-based QD coating.

Key words: quantum dots, lipids, photosensitizer, porphyrin, energy transfer

Abbreviations: QD – quantum dot, AlPcS4 – aluminium phthalocyanine tetrasulphonate, Ce6 – chlorin e6, TC1PP – 5-(4-carboxyphenyl)-10,15,20-triphenyl-21H,23H-porphine, TS1PP – 5-(4-sulphonatophenyl)-10,15,20-triphenyl-21H,23H-porphine, TC4PP – meso-tetra(4-carboxyphenyl)porphine, TS4PP – meso-tetra-(4-sulphonatophenyl)porphine, PB – phosphate buffer, DMSO – dimethyl sulfoxide, R_0 – distance between the QD and the porphyrin molecules for which the efficiency of energy transfer is 50%, Φ_D – quantum yield of QD emission, E – FRET efficiency between QD and porphyrin, J – spectral overlap integral of QD emission and porphyrin absorbance, R_0 – "Förster distance" at which the efficiency of transfer is 50%, r – distance between QD and porphyrin within a complex.

INTRODUCTION

Highly photoluminescent semiconductor quantum dots (QD) are intensively studied as promising materials for numerous biological and medical applications. Lately, it has been suggested that QD could be used in the photodynamic therapy (PDT) of cancer as resonance energy donors for conventional photosensitizers (PS) [1], thus broadening the excitation range of PS and enhancing their excitation efficiency, thus leading to a higher efficacy of PDT. The nature of QD and PS interaction plays a crucial role in the stability, photophysical properties and further effectiveness of such QD-PS complex. In previously reported studies on water-soluble QD and porphyrin complexes [2–6], the formation of a QD–porphyrin complex was driven mainly by electrostatic interaction, but the aggregation of such complexes arose as the main instability problem [3, 5, 7]. In this work, we demonstrate the possibility of producing a stable non-covalent QD–porphyrin

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complex whose formation is driven by the hydrophobic interaction between amphiphilic porphyrins and the lipid part of the QD coating. We have used commercial CdSe/ZnS quantum dots (eFluor NC, λ_{em} = 605 nm),) bearing a lipid-based coating with terminal carboxyl groups and different anionic porphyrin-type photosensitizers: aluminium phthalocyanine tetrasulphonate (AlPcS4), chlorin e_6 (Ce6), carboxyphenyl- and sulphonatophenyl-porphyrins with one (TC1PP, TS1PP) and four (TC4PP, TS4PP) functional carboxyl or sulphonate groups, respectively.

MATERIALS AND METHODS

CdSe/ZnS-carboxyl (605 nm) quantum dots (eFluor NC) (10 µM) were purchased from eBioscience (USA). Aluminium phthalocyanine tetrasulphonate, chlorin e_6, sulphonatophenylporphyrins with one and four functional sulphonate groups were obtained from Frontier Scientific Inc. (USA). Carboxyphenylporphyrins with one and four functional carboxyl groups were obtained from TCI Europe (Japan). Initial solutions of porphyrins were prepared in dimethylsulfoxide (DMSO) and further titrated with 5 µl to 2 ml of QD solution. The latter was prepared in a phosphate buffer at pH 7.0 (0.036M KH_2PO_4, 0.02M NaOH) (PB). In mixed QD-porphyrin solutions, the concentration of QD was 0.02 µM, while porphyrin concentration varied from 0.002 µM to 0.4 µM (molar ratios QD : porphyrin varied from 1 : 0.1 to 1 : 20). The spectra of QD-porphyrin complexes were measured 20 minutes after QD and porphyrin solutions had been mixed, allowing the binding of components to reach the equilibrium. The identical procedure was repeated for a control experiment which involved porphyrin without the presence of QD. Control measurements of QD were performed by titrating 2 µl PB (pH 7.0) instead of a porphyrin solution.

The steady state absorption and the fluorescence spectra of samples were recorded with a Cary 50 UV-Vis spectrophotometer (Varian, Inc., USA) and a Cary Eclipse fluorescence spectrophotometer (Varian, Inc., USA), respectively. Quartz cuvettes with the optical path length of 1 cm were used for the absorption and fluorescence measurements.

The quantum yield (QY) of photoluminescence of QD was calculated by comparison with rhodamine B in water (QY = 31%) at λ_{ex} = 514 nm [8].

The efficiency of fluorescence resonance energy transfer (FRET) between QD and porphyrins was calculated from the decrease of QD (donors) photoluminescence in the presence of porphyrins (acceptors):

$$E = 1 - \frac{F_D^{'}}{F_D}, \tag{1}$$

where F_D and $F_D^{'}$ are the intensities of QD photoluminescence in the absence and in the presence of porphyrin, respectively. For these calculations, the emission spectra of QD registered at the excitation wavelength at 465 nm were used. The level of decrease in QD emission intensity due to the dilution ef-

fect was encountered in the control measurements in which instead of porphyrins, pure PB was titrated to QD solution.

According to the Förster formalism [9], FRET efficiency is related to the distance between the donor and acceptor pair (r) by Eq. (2):

$$E = \frac{R_0^6}{R_0^6 + r^6}, \tag{2}$$

where R_0 is a "Förster distance" at which the efficiency of transfer is 50%. R_0, which is dependent on the spectral properties and relative orientation of the donor–acceptor pair, was evaluated from

$$R_0 = 0.211 \, (k^2 n^{-4} \, \Phi_D J \, (\lambda))^{1/6}, \tag{3}$$

where J is the spectral overlap integral of QD emission and porphyrins' absorbance, Φ_D is the quantum yield of the QD photoluminescence, n is the refractive index of the medium (taken to be 1.33), and κ^2 is a dipole orientation factor. The value of 2/3 for κ^2 was used on the basis of the assumption of random orientation of the QD and porphyrins upon binding. The overlap integral was approximated by Eq. 4:

$$J = \frac{\sum F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 \Delta\lambda}{\sum F_D(\lambda)\Delta\lambda}, \tag{4}$$

where F_D is the emission spectrum of QD, ε_A is the molar extinction coefficient of porphyrins, and λ is the wavelength in nanometers. The terms were summed over 1-nm intervals. The distance between QD and porphyrin (r) in a QD-porphyrin complex was calculated from Eq. (2).

The quantum yield of QD was calculated by comparison with Rhodamine B in water (Q_R = 31% at λ_{ex} = 514 nm):

$$Q = Q_R \frac{F}{F_R} \frac{OD_R}{OD} \frac{n^2}{n_R^2}, \tag{5}$$

where F and F_R are the integrated emission intensities of QD and Rhodamine B, respectively; OD and QD_R are its optical densities, respectively; n is the refractive of the medium.

The FRET parameters for QD–porphyrin complexes are summarized in Table.

RESULTS AND DISCUSSION

Structural and spectral properties of QD and porphyrin analogues

The schematic structure of QD used in this study is shown in Fig. 1. The hydrophobic CdSe/ZnS core is encapsulated in a micelle composed of amphiphilic phospholipid-n-poly(ethylene glycol) (PL-PEG) terminated with carboxyl groups [10]. It is well established that QD coated with a phospholipid block–copolymer micelle have a high quantum yield of photoluminescence and display a great reduction of photobleaching and colloidal stability in a variety of bioenvironments [11]. As shown in Fig. 2, QD have a broad absorption spectrum with pronounced excitonic peaks at around 555

Table. Fluorescence properties of porphyrins in PB, DMSO and upon binding to QD and FRET characteristics of QD-porphyrin complexes

| Porphyrin	Fluorescence maximum of porphyrin[1], nm			QD-porphyrin complex (c_{QD} = 0.02 μM, QD : porphyrin, 1 : 1)			
	PB	DMSO	In the presence of QD (c_{QD} = 0.02 μM, QD : porphyrin, 1 : 1)	E, %	J, $M^{-1}cm^{-1}nm^4$	R_0, nm	r, nm
AlPcS4	680	690	680	1	$5.6 \cdot 10^{15}$	4.9	13.8
Ce6	660	670	670	14	$3.8 \cdot 10^{13}$	2.1	4.2
TC1PP	653, 722	650, 715	650, 715	14	$9.6 \cdot 10^{13}$	2.5	5.0
TC4PP	645, 705	650, 715	650, 715	2	$2.8 \cdot 10^{14}$	3.0	8.4
TS1PP	656, 720	650, 717	652, 717	11	$1.7 \cdot 10^{14}$	2.8	5.7
TS4PP	643, 705	650, 717	645, 705	1	$4.2 \cdot 10^{14}$	3.2	10.1

[1]λ_{ex} = 465 nm.
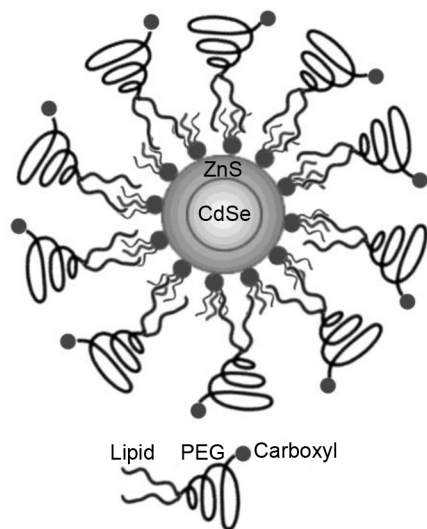
Fig. 1. Schematic structure of QD. CdSe nanocrystal core is capped with ZnS shell which not only increases the stability and emission quantum yield, but also reduces the toxicity of the core by shielding reactive Cd^{2+} ions from being exposed to the environment. However, a ZnS shell is not sufficient to stabilize the CdSe core in aqueous solutions, and therefore a further coating is required to ensure solubility in aqueous media. In our case, QD is encapsulated in phospholipid micelles with attached poly(ethylene glycol) (PEG) polymers and terminal carboxyl groups. PEG polymer ensures nonimmunogenicity and nonantigenicity of nanoparticles in the organism

and 595 nm. The photoluminescence spectrum of QD displays a narrow band at 605 nm. The calculated quantum yield (Φ_D) of QD photoluminescence was ~20% (λ_{ex} = 465 nm). Since the photoluminescence band of QD overlapped with the absorption spectrum (Q bands) of all used porphyrins, the main condition for the resonance energy transfer from QD (donor) to porphyrins (acceptors) was fulfilled. The other requirement for an efficient FRET is the proximity of energy donor and acceptor within a distance less than 10 nm. The manufacturer provided that the diameter of the spherical QD emitting at 605 nm was 4.3 nm without coating [12]. However, the results of dynamic light scattering, obtained by the manufacturer, indicated that the hydrodynamic radius of eFluor QD ranged from 10 to 13 nm [13]. Other authors using QD of a similar type reported the range of the hydrodynamic diameters from 15 to 23 nm [10]. Thus, such size of QD is marginal for FRET, if the binding of porphyrins occurs on the exterior of QD coating. In addition, FRET depends on the relative orientation of partners due to the dipole–dipole nature of the resonance energy transfer mechanism. However, this parameter is often difficult to evaluate.

The structure of porphyrin-type photosensitizers tested in this work is shown in Fig. 3. Three of them have a hydrophilic character due to four polar groups, either sulphonate (AlPcS4, TS4PP) or carboxyl (TC4PP), symmetrically positioned on each phenyl ring. The rest of porphyrins exhibited
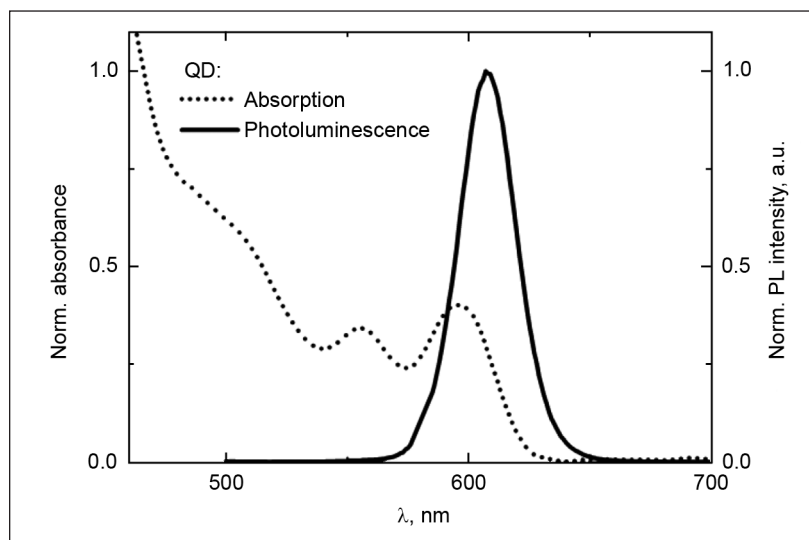

Fig. 2. Normalized absorption and emission spectra of 0.02 μM QD solution (PB pH 7.0). Excitation wavelength 465 nm
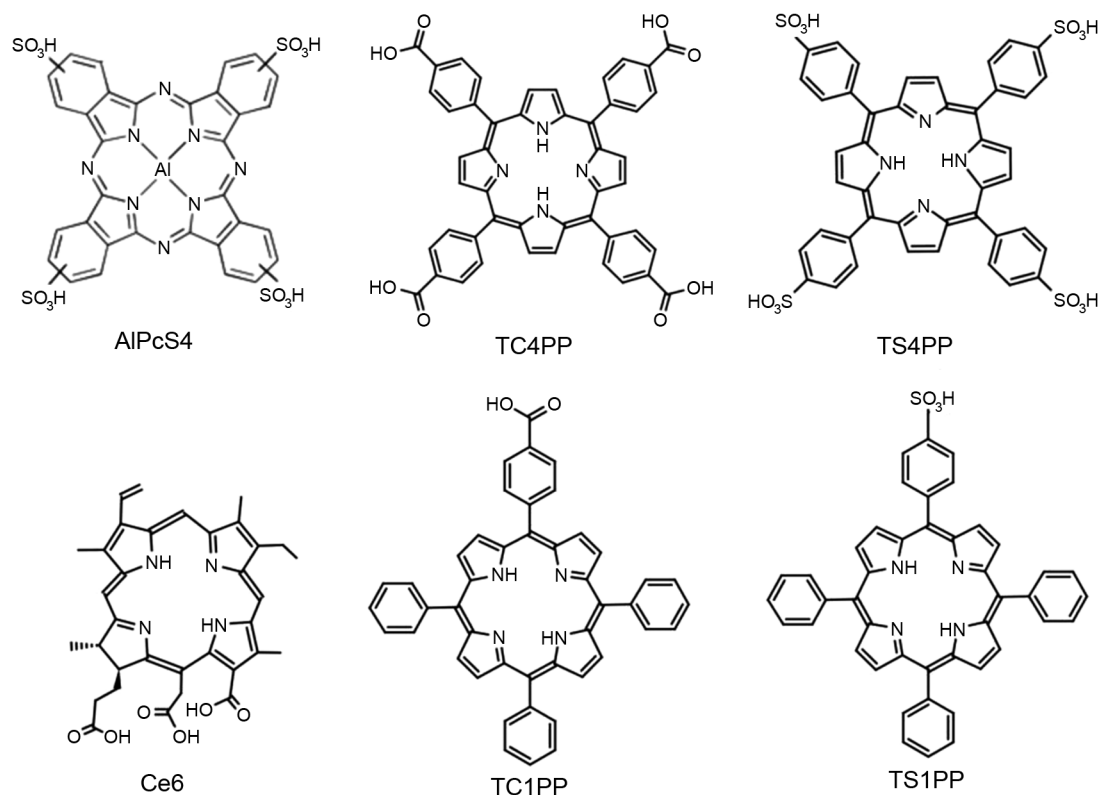
Fig. 3. Molecular structure of porphyrin-type photosensitizers used in this work. AlPcS4 – aluminium phthalocyanine tetrasulphonate; Ce6 – chlorin e6; TC4PP and TC1PP – carboxyphenyl porphyrins with four and one carboxyl groups, respectively; TS4PP and TS1PP – sulphonatophenyl porphyrins with four and one sulphonate groups, respectively

an amphiphilic character since their polar group(s) was (were) situated only on one side of the porphine macrocycle (Ce6, TC1PP and TS1PP).

The absorption, fluorescence excitation and fluorescence spectra of each porphyrin in the absence and in the presence of QD are shown in the first, second and third columns of Fig. 4, respectively. The spectra of porphyrins in amphiphilic solvent DMSO are also given and compared with those obtained in the presence of QD.

Interaction of AlPcS4 with QD

Since the chemical structure of AlPcS4 and Ce6 is dissimilar to the rest of the investigated porphyrins, their spectra are also distinct from that of the other porphyrins.

The absorption spectrum of AlPcS4 consists of the Soret band at 350 nm and a much more intensive Q band at 675 nm (Fig. 4A). The fluorescence band maximum of AlPcS4 in PB is at 680 nm (Fig. 4C). In DMSO, the absorption and fluorescence bands of AlPcS4 are shifted bathochromically by 10 nm (Fig. 4 A and C, respectively). Addition of AlPcS4 to QD solution resulted in a slight quenching of QD emission intensity and a simultaneous increase in the fluorescence intensity of phthalocyanine (Fig. 4C). When the excitation at 465 nm was used, at which AlPcS4 absorbance is minimal and therefore the direct excitation of AlPcS4 is negligible, the intensity of AlPcS4 fluorescence in the presence of QD was about seven

times higher than in a pure PB solution (Fig. 4C, inset). These findings indicate energy transfer from QD to AlPcS4. In the fluorescence excitation spectrum registered at AlPcS4 fluorescence maximum (680 nm), a minor contribution of QD spectrum was obtained (Fig. 4B). However, in the presence of QD, the emission maximum of AlPcS4 was observed at the same position as in PB (680 nm) and did not shift to 690 nm as in DMSO. This suggests that AlPcS4 molecules in the presence of QD remained in the aqueous medium. The efficiency of energy transfer calculated from the quenched photoluminescence intensity of QD after the addition of AlPcS4 was only 1% (Table). The evaluated distance between QD and AlPcS4 was even larger than the QD radius – 13.8 nm. This implies that AlPcS4 molecules remain on the exterior of QD, and a minor energy transfer occurs most likely via a dynamic interaction of QD with AlPcS4.

Formation of stable QD–Ce6 complex

Quite a different profile of interaction with QD was observed for amphiphilic Ce6 molecules. The absorption, fluorescence excitation and fluorescence spectra of Ce6 are shown in Fig. 4 D, E and F, respectively. The absorption spectrum of Ce6 in PB exhibits a Soret band at 403 nm and a Q (I) band at 654 nm. The fluorescence maximum of Ce6 is at 660 nm. The absorption properties of Ce6 were less favourable for energy transfer from QD to occur in comparison with AlPcS4 due to
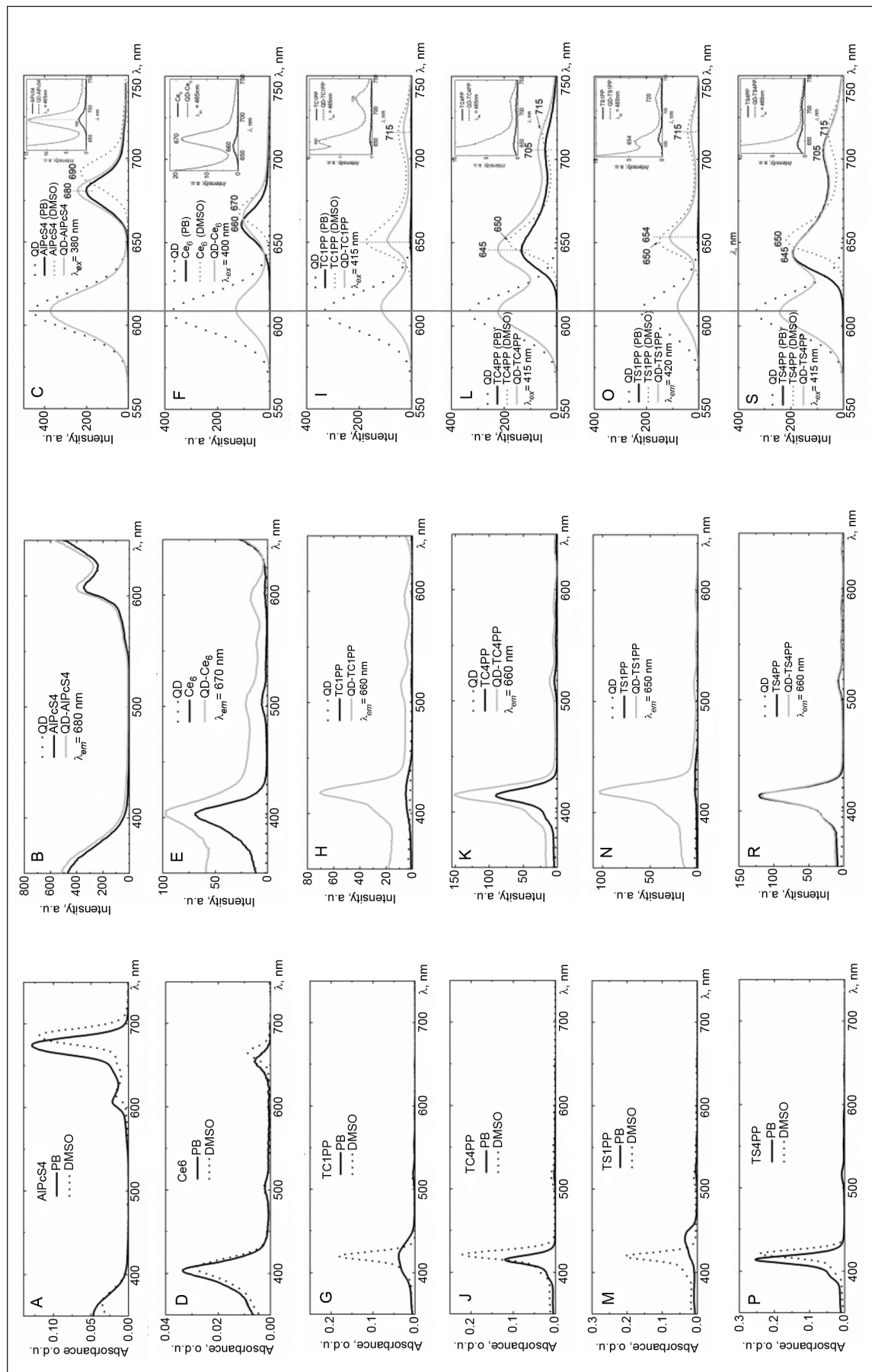
Fig. 4. Absorption (A, D, G, J, M, P), emission excitation (B, E, H, K, N, R) and emission (C, F, I, L, O, S) spectra of different porphyrins (0.4 µM) without and with QD (molar ratio of QD : porphyrin, 1 : 20, c_{QD} = 0.02 µM) in PB (pH 7.0). For comparison, the absorption and emission spectra of porphyrins at a corresponding concentration in DMSO are also shown. Insets show emission spectra of porphyrin solutions without and with QD at 465 nm excitation

a less extent of the overlap with the QD photoluminescence band (see overlap integrals (J) in Table). However, the increasing concentration of Ce6 produced a much higher decrease in QD photoluminescence intensity than in case of AlPcS4. When using the excitation wavelength at 465 nm, at which the direct excitation of Ce6 was minimal, the intensity of Ce6 fluorescence in the presence of QD was ten times higher than in pure PB. Moreover, the fluorescence band of Ce6 in the presence of QD displayed the maximum at 670 nm (Fig. 4F, inset), which was red-shifted by 10 nm as compared with that in PB but similar to that observed in DMSO (Fig. 4F). A significant contribution of the QD spectrum was seen in the fluorescence excitation spectrum registered at the Ce6 emission maximum (670 nm) in mixed QD-Ce6 solution (Fig. 4E). When the molar ratio QD : Ce6 increased to 1 : 20, the fluorescence band of free Ce6 (660 nm) became dominant at 400 nm excitation. This indicates that the number of bound Ce6 molecules per QD might be more than 10. All the above findings imply QD–Ce6 complex formation with the ability of energy transfer from QD to bound Ce6 molecules. The calculated efficiency of energy transfer within the QD–Ce6 (QD : Ce6, 1 : 1) complex was 14%, and the distance between QD and Ce6 was 4.2 nm (Table). Taking into account the information that the hydrodynamic radius of coated QD is larger than 10 nm [13], bound Ce6 molecules must be localized inside the coating of QD. The resemblance of the Ce6 fluorescence spectrum in amphiphilic DMSO to the respective spectrum of Ce6 bound to QDs (Fig. 4F) confirms the presumption that, upon binding, Ce6 molecules appear in the microenvironment of similar polarity. An analogous bathochromic shift of Ce6 fluorescence maximum to 670 nm has been reported when Ce6 was incorporated into a lipid bilayer [14, 15]. It has been shown also by using artificial phospholipid vesicles that Ce6 molecules localize within a lipid bilayer by protruding the hydrophobic core of the porphyrin macrocycle into the nonpolar membrane interior while the polar carboxyl groups orient towards the aqueous phase [14–16]. Thus, taking into account all these facts, we can deduce that Ce6 molecules are immersed in the hydrophobic part of lipid molecules of the QD coating. This brings Ce6 close enough to a QD core / shell for the energy transfer from QD to occur.

Binding of tetraphenylporphyrins to QD

Depending on their structure, the other porphyrins acted with QD in accordance with the interaction models described either for hydrophilic AlPcS4 or amphiphilic Ce6 molecules. Since the structure of tetraphenylporphyrins varied only in the type and number of polar groups, the differences in their spectral properties had to be minimal. However, in PB the absorption (Fig. 4 J, P) and fluorescence (Fig. 4 P, S and Table) spectra matched only between porphyrins with four polar groups, TC4PP and TS4PP, respectively. The spectra of porphyrins with one polar group displayed a highly reduced absorbance (Fig. 4 G, M) and a low intensity of fluorescence (Fig. 4 I, O). Moreover, the absorption and fluorescence bands

of TC1PP and TS1PP were bathochromically shifted in respect to the corresponding spectra of TC4PP and TS4PP (Table). However, if DMSO was used instead of PB, the absorption and fluorescence spectra of all porphyrins perfectly coincided (Fig. 4 G, J, M, P and Table). This might be explained by the monomerization of amphiphilic TC1PP and TS1PP in DMSO. The aggregation of tetraphenylporphyrins in an aqueous medium of different pH was reported in numerous studies [17–21]. In the presence of QD, TC1PP and TS1PP displayed a similar position of fluorescence band as in DMSO (Fig. 4 I, O). This indicates that upon binding to QD these porphyrins were located in a non-polar environment as in the case of Ce6 and here their monomerization occurred. The binding of porphyrins to QD resulted in a decrease of QD emission intensity and a significant increase in fluorescence intensity of bound porphyrins (Fig. 4 I, O). In the presence of QD, the fluorescence excitation spectra of TC1PP (Fig. 4H) and TS1PP (Fig. 4N) contained the contribution of QD spectrum. The calculated efficiency of energy transfer for the QD–TC1PP complex (14%) was by a few percent higher than for QD-TS1PP (11%) (Table), and the distance within the complex was also slightly shorter in the case of TC1PP (Table). However, the shortest distance was obtained within the QD–Ce6 complex. This suggests that amphiphilic porphyrins containing carboxyl groups interact with QD more effectively than do sulphonate porphyrins. The interaction of QD with tetraphenylporphyrins bearing four polar groups spectrally was much less pronounced (Fig. 4 L, S). Interestingly, in the case of QD-TC4PP, the small fraction of TC4PP molecules was excited via FRET from QD (λ_{ex} = 465 nm) (Fig. 4L, inset) and displayed similar fluorescence maxima as in DMSO or bound TC1PP (Table). This reveals that, despite the hydrophilic nature, a few TC4PP molecules have penetrated into the lipid part of the QD coating. However, the efficiency of energy transfer from QD to TC4PP molecules was only 2% and, subsequently, the overall distance exceeded 8 nm (Table). The least spectral changes in the presence of QD were obtained for tetraphenylporphyrin with four TS4PP sulphonate groups. Although the addition of TS4PP produced a slight decrease in QD emission intensity, no changes either in the fluorescence intensity or in spectral shifts were observed for TS4PP itself (Fig. 4S). The efficiency of energy transfer from QD to TS4PP was only 1% (Table). As in the case of AlPcS4, the energy transfer from QD to TS4PP most likely occurs via a dynamic interaction, i. e. without the formation of a stable complex.

CONCLUSIONS

These results provide a direct evidence of a stable non-covalent complex formation between QD bearing a lipid-based coating and amphiphilic porphyrins, with the ability to undergo FRET. A model of the interaction between QD and porphyrins is proposed. Based on spectral results, it can be assumed that amphiphilic porphyrins incorporate into the hydrophobic interior of the lipid part of QD coating. This en-

sures a close localization of porphyrins to the QD core / shell for FRET to occur. Further studies on the photosensitizing properties, such as ROS generation, of such QD–porphyrin complexes are required to reveal their possible practical applications.

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KOMPLEKSO TARP SKIRTINGŲ PORFIRINŲ IR KVANTINIŲ TAŠKŲ, PADENGTŲ LIPIDINIU APVALKALU, SUSIDARYMO SPEKTROSKOPINIAI TYRIMAI

S a n t r a u k a

Šiame darbe tirtas komplekso tarp kvantinių taškų ir skirtingų anijoninių porfirinų susidarymas vandeninėje terpėje taikant nuostoviosios spektroskopijos metodus. Tyrimo metu buvo naudojami CdSe / ZnS komerciniai kvantiniai taškai, padengti lipidiniu apvalkalu su išorinėmis karboksi- grupėmis. Buvo nustatyta, kad amfifiliniai porfirinai – chlorinas e_6, karboksifenil- ir sulfonatofenilporfirinai, turintys vieną polinę grupę, jungiasi prie kvantinių taškų, sudarydami stabilų kompleksą, kuriame energija pernešama iš kvantinio taško į prisijungusias porfirino molekules. Energijos pernašos iš kvantinių taškų į prisijungusius amfifilinius porfirinus efektyvumas siekė nuo 11 iki 14 %. Prie kvantinių taškų prisijungusių karboksifenilporfirinų (Ce6, TC1PP) spektriniai pokyčiai ir energijos pernašos efektyvumas buvo didesni negu sulfonatofenilporfirino (TS1PP). Sumaišius kvantinius taškus su porfirinais, turinčiais keturias polines grupes, pastebėti tik nereikšmingi spektriniai pokyčiai, o energijos pernašos efektyvumas tesiekė kelis procentus. Remiantis gautais rezultatais galima teigti, kad susidarant kompleksui, amfifiliniai porfirinai nepoline dalimi panyra į kvantinių taškų apvalkalo lipidus.

Raktažodžiai: kvantiniai taškai, lipidai, fotosensibilizatoriai, porfirinai, energijos pernaša