ISSN 0006-2979, Biochemistry (Moscow), 2012, Vol. 77, No. 6, pp. 624-630. © Pleiades Publishing, Ltd., 2012.
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Hybrid System Based on Quantum Dots and Photosystem 2 Core Complex

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Received February 28, 2012
Revision received March 16, 2012

Abstract—We show that semiconductor nanocrystals (quantum dots, QD) can be used to increase the absorption capacity of pigment–protein complexes. In a mixture of photosystem 2 core complex (PS2) and QD, the fluorescence of the latter decreases several-fold due to the transfer of the absorbed energy to the PS2 core complex. We discuss Forster's inductive-resonance mechanism as a possible way of energy transfer in donor–acceptor pairs QD–PS2 core complex. Calculations based on the experimental data show that the enhancement of PS2 fluorescence and the rate of Q_A reduction increase up to 60% due to efficient energy migration from QD to PS2.

DOI: 10.1134/S0006297912060090

Key words: quantum dots, photosystem 2, hybrid systems, energy transfer

The primary processes of photosynthesis in cyanobacteria, algae, and higher plants occur in thylakoid membranes, which contain transmembrane protein complexes of photosystem 2 (PS2), cytochrome b_6f, and PS1. Light-induced oxidation of water and release of molecular oxygen are catalyzed by PS2 complex, which is an H_2O-plastoquinone-oxidoreductase whose functioning mechanism is still the subject of intensive research [1, 2]. As a result of charge separation and vectorial electron transfer, transmembrane electrical potential difference ($\Delta\Psi$), which is the primary form of membrane energy storage, is formed both at the donor and the acceptor sides of the enzyme [3-5]. It is known that the efficiency of charge separation in photosynthetic reaction centers (RC) is close to 100% [6]. The high quantum yield of the primary ion-radical pair formation in RC suggests reaction centers as possible photoconverters of light energy into electrical energy. Calculations show that with use of these natural "generators" photoconverter efficiency can be significantly higher than that of the best modern solar cells [7]. The core idea of the hybrid energy photoconverter is to use systems such as photosynthetic reaction center–molecular conductor–macroscopic electrode to produce an electric current [8]. However, the small optical density of thin layer of isolated reaction centers applied to the electrode casts doubt on the effectiveness and feasibility of such devices [9]. This problem can be solved by the creation of artificial multi-component energy converting devices that can effectively absorb the solar energy and convert it into electrochemical potential.

Modern nanotechnology allows the preparation of semiconductor nanocrystals, or so-called quantum dots (QD), which absorb light in a broad optical range from ultraviolet to near infrared. The fluorescence spectrum of QDs is rather narrow (spectral width at half-height 20-25 nm), is ideally symmetric, and the position of their maximum fluorescence emission is determined by the diameter of the nanocrystal particle [10]. While being slightly worse than the best fluorescent labels in the magnitude of fluorescence quantum yield (~70% at room temperature), quantum dots exceed them by several orders of magnitude in light absorption cross-section [11]. Additional organic coating of bi- or trifunctional polymers provides water solubility to nanocrystals due to surface polar groups [12, 13]. Functional groups of organic coating are available for conjugation, which makes it possible to create artificial light-harvesting complexes based on quantum dots, which can serve as highly

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effective energy donors for photosynthetic pigment–protein complexes [14].

The structure of core PS2 complex containing two antenna proteins CP43 and CP47, reaction center (D1/D2/cytochrome b_{559}), and a number of low molecular weight proteins (about 15) was revealed by X-ray analysis of crystals from thermophilic cyanobacteria with resolution of 1.9 Å [15]. All major components of PS2 electron transport chain – primary electron donor P680, electron carriers in the acceptor chain (chlorophyll *a* monomer, pheophytin *a*, primary (Q_A) and secondary (Q_B) quinone acceptors), and electron carriers on the donor side (redox-active amino acid residue tyrosine Y_Z and Mn_4Ca-cluster) – are located on D1 and D2 proteins of RC [15]. Core complexes of PS2 contain a minimum number of chlorophyll *a* molecules (35-50) and retain the ability for photoinduced release of molecular oxygen [16]. In addition, these complexes display characteristic induction of chlorophyll fluorescence [17]. Therefore, these complexes are PS2 photoactive particles with the smallest antenna and can serve as a convenient object for the study of hybrid structures.

We previously established experimentally that quantum dots, used as additional artificial light collectors, efficiently absorb light in the ultraviolet and visible regions of the spectrum and transmit energy to native photosynthetic pigment–protein complex (PPC) [18-20]. The aim of this study was to investigate hybrid systems of quantum dots and core complexes of PS2. It was found that quantum dots and PS2 core complexes are capable of forming a hybrid structure with highly efficient transfer of excitation energy from QD to PS2. Energy transfer from QD can significantly increase light collection of PS2 core complexes in the ultraviolet and visible regions. It is shown that the increase of PS2 core complex absorption after formation of hybrid structures with quantum dots leads to an increase in the rate of the primary electron acceptor reduction. In effect, this means that the energy conversion efficiency of the hybrid system QD + PS2 approaches the efficiency of the native complex of PS2 + light-harvesting complexes (LHC).

MATERIALS AND METHODS

Core complexes of PS2 were isolated from PS2-enriched membrane fragments from spinach in the presence of glycine betaine [21] using the method described in [22]. Concentrated suspension of core PS2 complexes was resuspended for measurements in 50 mM MES buffer containing 1 M betaine, 300 mM sucrose, and 15 mM NaCl.

Comparison of the spectral properties of quantum dots and PS2 core complexes allowed the construction of a hybrid system in such a way as to ensure strong overlap of the fluorescence spectra of energy donor (QD) and energy acceptor (PS2). Water-soluble (due to the presence of a hydrophilic coating with carboxyl groups) quantum dots QD 630 (digital code corresponds to QD maximum fluorescence intensity at 630 nm) with a diameter of CdSe/ZnS crystal of 5.2 nm were selected (NanoFluorescent Materials LTD, Ukraine) [13]. A schematic structure of the hybrid complex QD + PS2 is shown in Fig. 1 (see color insert).

Optical absorption spectra were recorded with Hitachi-557 (Japan) and Ocean Optics (USA) spectrophotometers. To register fluorescence spectra of emission and excitation, we used a Horiba Jobin Yvon FluoroMax-4 spectrofluorimeter (France) [19]. Fluorescence emission spectra were recorded in the range from 400 to 800 nm with excitation at 266 and 355 nm. Fluorescence induction curves were measured with instruments Handy-PEA (Plant Efficiency Analyzer) Hansatech (UK) with excitation light wavelength of 655 nm [23] and high temporal resolution fluorimeter developed by the Department of Biophysics, Biological Faculty, Moscow State University, with maximum intensity of excitation light at 455 nm [24]. Each experiment was repeated at least five times.

RESULTS AND DISCUSSION

Spectral characteristics of the hybrid complex components – QD and PS2 – are shown in Fig. 2. Fluorescence emission spectrum of the QD and the absorption spectrum of PS2 core complexes allowed us to calculate the overlap integral $I = \int_0^\infty F_d(\lambda)\varepsilon_a(\lambda)\lambda^4 d\lambda$, the value of which was $1.67 \cdot 10^{-13}$ cm^6. The following denotations were used in the equation for I: $F_d(\lambda)$, normalized fluorescence spectrum of energy donor; $\varepsilon_a(\lambda)$, molar extinction coefficient of acceptor; λ, wavelength. The Forster radius R_0 of the interacting components of QD and PS2 was calculated from the equation:

$$R_0 = [8.8 \times 10^{-25}(k^2 n^{-4} \varphi_d I)]^{1/6},$$

where φ_d, fluorescence quantum yield of the donor in the absence of the acceptor; n, refractive index of the medium; k^2, the factor which takes into account the relative orientation in space of transition dipole moments of donor and acceptor, which was considered equal to 2/3 [25, 26]. It was found that the calculated value R_0 for the QD 630–core PS2 complex system was 58.2 Å. Obviously, either approach of donor and acceptor molecules in the solution by distance on the order of R_0 due to thermal motions or the formation of hybrid protein–QD complexes are needed for non-radiative energy transfer from the QD to the PS2.

In this study, a series of experiments was carried out that evaluated the spectral characteristics of quantum dot solutions (energy donor) with fixed concentration, to

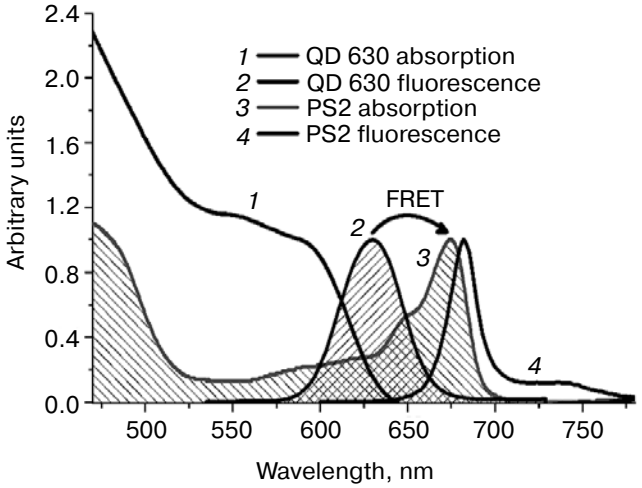

Fig. 2. Spectra of optical absorption (*1*, *3*) and fluorescence emission (*2*, *4*) of the PS2 core complexes (*3*, *4*) and quantum dots QD 630 (*1*, *2*). The spectra are normalized to the corresponding values of the intensity maxima of absorption/fluorescence. The arrow (FRET) indicates possible transfer of electronic excitation energy from QD 630 to PS2.

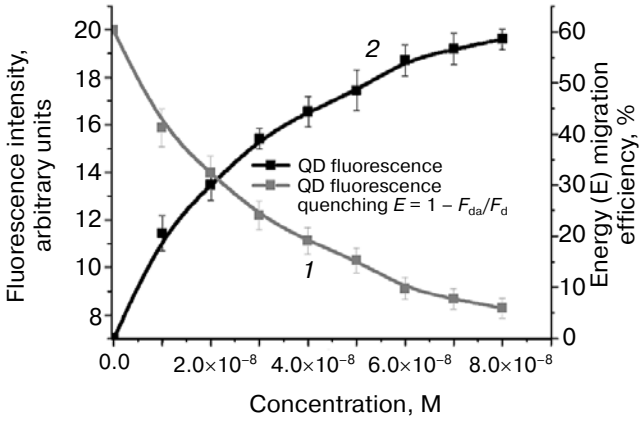

Fig. 3. Effectiveness of fluorescence quenching of QD 630 (*1*) and energy migration from QD to core complexes of PS2 (*2*). The efficiency of energy migration $E = 1 - F_{da}/F_d$ (curve *2*) is calculated from analysis of QD fluorescence intensity changes. Excitation wavelength of the binary system was 355 nm.

which various concentrations of PS2 core complexes (energy acceptor) were added. Analysis of the fluorescence spectra showed the classic changes characteristic of donor–acceptor interactions in these two-component solutions – a decrease in the intensity of energy donor QD intrinsic fluorescence (Fig. 3) and an increase in fluorescence intensity of acceptor – core complexes of PS2 (Fig. 4).

We used very low concentrations of QD and PS2 core complexes in these experiments (10^{-11}-10^{-8} M). If we assume that molecules are distributed uniformly in the solution, then the average distance between donor and acceptor at the concentrations used in the experiments is several hundred nanometers, which is significantly greater than the calculated value of Forster radius R_0 = 58.2 Å. Consequently, at the chosen concentrations and given a random arrangement of QD and proteins in solution, energy transfer should not occur. In addition, under these conditions fluorescence reabsorption is also negligible, and therefore the control experiment showed a linear dependence of the intensity of chlorophyll fluorescence on the concentration of PS2 core complexes (Fig. 4). Since the molecular weights and diameters of QD and core complexes of PS2 are known, it is easy to estimate the frequency of particle collisions in a binary solution using the equations of the theory of active collisions [27]. Calculations show that no more than 5-15 collisions per second occur at these concentrations (at room temperature) in the volume of study (i.e. in which the excitation of fluorescence occurs). However, there are about 10^9 donor–acceptor pairs in this volume, so it is reasonable to assume that if the energy transfer from quantum dots to core complexes of PS2 does occur, it is not due to the diffusion approach of energy donor and acceptor and reabsorption of fluorescence, but because of the formation of hybrid complexes. In this case the energy transfer takes place nonradiatively (by the inductive-resonance mechanism).

Figure 4 (curve *2*) shows that the binary system demonstrates chlorophyll fluorescence growth in the optimal range of concentrations of QD and core complexes of PS2. Therefore, QD and core complexes of PS2 form interacting complexes (hybrid systems) in which efficient energy transfer from QD to PS2 takes place. The QD used in this study has a characteristic feature – negatively charged carboxyl groups on the outer surface of the

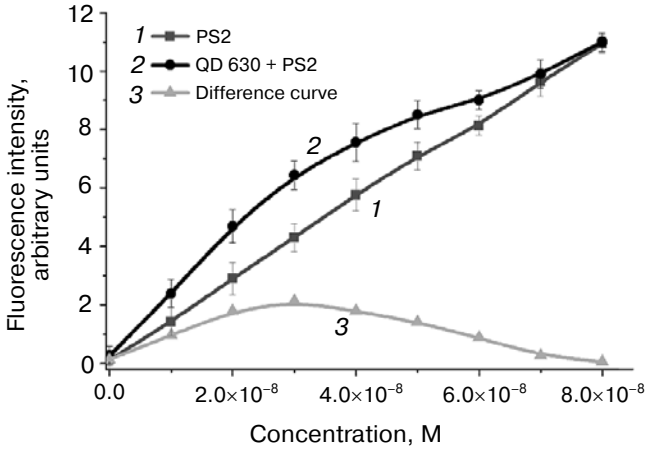

Fig. 4. Dependence of fluorescence intensity at 685 nm (fluorescence spectrum maximum of PS2 core complexes) on the concentration of PS2 without (*1*) or with addition of QD 630 (*2*). The wavelength of fluorescence excitation was 355 nm; *3*) difference curve.

shell. As the protein structure of the PS2 core complex contains positively charged amino acid residues [15], we assume that QD form hybrid structures in mixed solutions with PS2 core complexes due to electrostatic interactions between negatively charged groups of the outer shell and the positively charged amino acid residues of the proteins.

Mathematical analysis of the fluorescence spectra allowed study of the dependence of quantum dot fluorescence quenching efficiency on the concentration of core complexes of PS2. A control experiment was conducted in which the concentration dependence of the spectral characteristics of PS2 core complexes solutions was identified and the range was determined in which the fluorescence intensity depends linearly on the concentration of the protein. To account for the overlapping of fluorescence spectra of energy donor and acceptor, we used appropriate correction factors [28]. It was found that fluorescence quenching of QD 630 reaches 50-60% at the highest concentrations of acceptor (Fig. 3). Since static quenching of QD fluorescence can take place in the studied system besides dynamic quenching [29], an increase in the fluorescence intensity of energy acceptor (PS2) may be the proof of energy migration. The fluorescence enhancement coefficient was calculated by the equation:

$$A = \frac{F_{ad} - F_a}{F_a},$$

where F_a is relative fluorescence quantum yield of the acceptor in the absence of a energy donor and F_{ad} is relative quantum yield of the acceptor in the presence of the donor (Fig. 5) [19]. The calculations showed that fluorescence enhancement coefficient (A) for the QD 630–PS2 pair reached values of 0.65 (see Fig. 5).

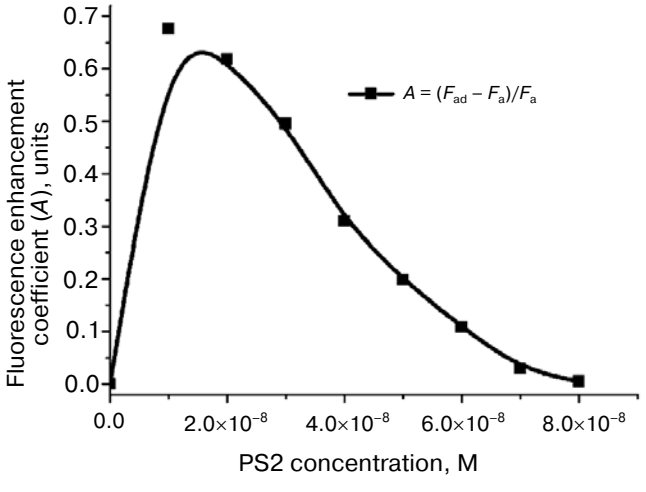

Fig. 5. Changes in fluorescence enhancement coefficient ($A = F_{ad} - F_a)/F_a$) of chlorophyll from PS2 complexes after addition of QD 630. Calculated from data in Fig. 4.

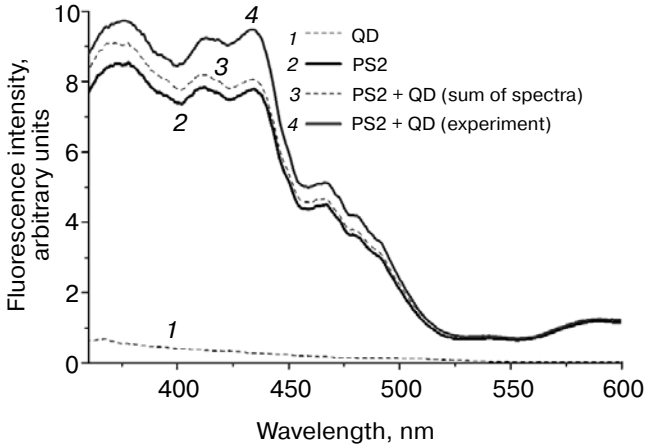

Fig. 6. Fluorescence excitation spectra of QD 630 (*1*), PS2 core complexes (*2*), and hybrid complexes of QD 630–PS2 (*3*). For comparison, the sum of the excitation spectra of solutions of QD and PS2 core complexes is shown (*4*). Fluorescence was recorded at 685 nm.

Similar results were obtained when comparing the fluorescence excitation spectra of individual solutions of PS2 core complexes, QD, and their mixture. In these experiments the luminescence intensity was recorded at a wavelength of maximum fluorescence of the acceptor PS2 (685 nm), both for actual QD and core complexes of PS2 in pure solutions and in binary systems with QD. As expected, the addition of QD leads to an increase in the fluorescence intensity of PS2, and this amplification occurs due to light absorption by QD 630 and the subsequent migration of energy (Fig. 6). Comparing the areas under the fluorescence excitation spectra (Fig. 6) also allowed us to estimate the gain coefficient of PS2 fluorescence due to energy migration from QD 630, the value of which amounted to 0.65. It should be noted that the QD effect was not observed in the fluorescence excitation spectrum of the PS2 nuclear complexes when protein concentrations were very high.

An alternative approach for determining the fluorescence enhancement coefficient of PS2 core complexes is to compare the rates of photochemical reactions products formation. It is known that chlorophyll fluorescence intensity growth from the minimum F_0 to the maximum F_m in the initial part of the curve of chlorophyll fluorescence induction characterizes the dynamics of photochemical reaction product accumulation [17, 30, 31]. In the analysis of fluorescence induction curves we used an approach based on the assumption that the first (fast) stage of the induction curve characterizes the reduction of Q_A (i.e. the transition of RC to "closed" state), and consequent stages characterize slow reduction of Q_B [30]. The initial part of fluorescence induction curve was approximated by a sum of exponentials:

$$X(t) = 1 - [B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2}],$$

where B_i is pre-exponential factors of the components and τ_i the corresponding times. Since τ_2 is greater than τ_1 by more than an order of magnitude, the exponential components of function $X(t)$ do not overlap in time and thus can be analyzed independently. It is known that the product yield of the photochemical reaction is proportional to the photon flux density of the exciting pulse I_0 and the effective cross section of PS2 RC fluorescence excitation σ_{PS2} [23]. In turn, σ_{PS2} equals the product of the effective cross section of absorption and fluorescence quantum yield. The share of PS2 RC in "closed" state can be defined as follows [30]:

$$X(t) = \frac{F(\tau) - F_0}{F_m - F_0} = 1 - e^{-\sigma_{PS2} I_o t},$$

where σ_{PS2} is effective cross section of fluorescence excitation, which was calculated according to the formula:

$$\sigma_{PS2} = 1/\tau_1 I_0,$$

where τ_1 is the characteristic time of the fast stage of PS2 chlorophyll fluorescence induction.

Estimation of energy migration efficiency is possible in the approximation in which constants of acceptor fluorescence rate and photochemical reactions rate do not depend on the energy migration rate constant, and excitation energy capture is accomplished by reaction centers (RCs) of PS2 with 100% efficiency. In these approximations, energy migration from QD (donor D) to the chlorophyll of PS2 core complex (acceptor A) and then to the RC [PQ] can be represented by the following scheme:

$$DA[PQ_A] + h\nu \xrightarrow{k_1} D^*A[PQ_A] \xrightarrow{k_m} DA^*[PQ_A] \xleftrightarrow{k'_m} \leftrightarrow DA[P^*Q_A] \xleftrightarrow{k_{PQ}} DA[P^+Q_A^-].$$

It is obvious that the accumulation rate of $P^+Q_A^-$ state depends on the concentration of acceptor A in the excited state (A*). It is also clear that energy migration from the donor to the acceptor leads to an increase in the number of acceptor molecules in the excited state and, therefore, to an increase in the rate of photoproduct formation. Since the effective excitation cross section of fluorescence is used to estimate the rate of reduction of Q_A, the fluorescence enhancement coefficient A can be calculated in this model by the following equation [23]:

$$A = \frac{\sigma_{PS2} + QD}{\sigma_{PS2}} - 1.$$

Analysis of fluorescence induction curves (Fig. 7) along the described methodology established that the addition of QD leads to an increase in the rate of PS2 fluorescence growth, which is, in fact, rate of reduction of the primary acceptor (Fig. 7). Analysis of chlorophyll fluorescence induction curves of PS2 core complexes allowed us to estimate the change in the effective fluorescence excitation cross section σ_{PS2} after addition of quan-

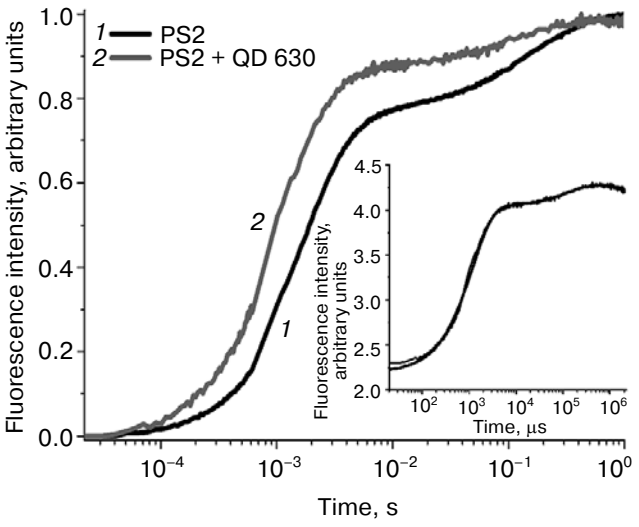

Fig. 7. Curves of fluorescence induction of PS2 core complexes (*1*) and hybrid systems of PS2 core complexes and QD 630 (*2*). Photon flux density of the excitation light was 1500 μE from an LED with maximum emission intensity at 455 nm. The inset shows the results of the induction curve approximating with function $X(t) = 1 - [B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2}]$.

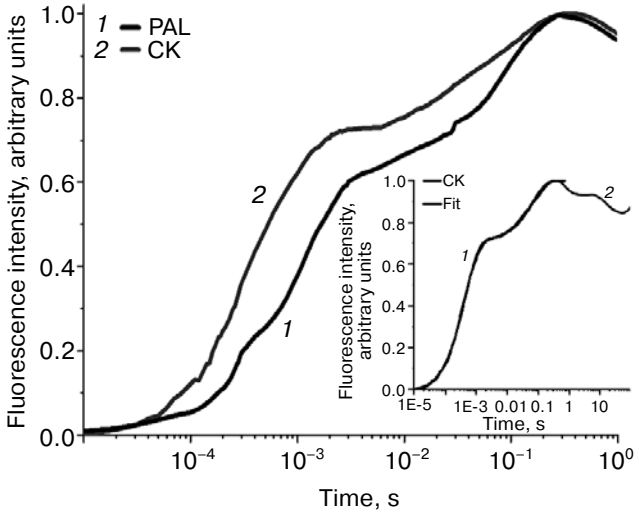

Fig. 8. Fluorescence induction curves of CK (*2*) and PAL (*1*) mutants of cyanobacterium *Synechocystis* sp. PCC6803 obtained with the Handy-PEA instrument (excitation at 655 nm). The inset shows the results of the induction curve approximation (*1*) with sum of two exponential functions (*2*).

tum dots and the corresponding coefficients of acceptor fluorescence growth *A*. Fluorescence growth coefficients obtained by measuring fluorescence induction reach values of 0.55-0.60 in good agreement with estimates obtained from the stationary fluorescence.

Use of QD as artificial antenna complexes can be promising only if they are able to provide efficiency of energy transfer to acceptors that is comparable to that in natural light collectors, for example, such as phycobilisomes of cyanobacteria. Previously, we investigated the fluorescence induction curves of the mutant of cyanobacterium *Synechocystis* sp. PCC 6803 PAL lacking phycobilisomes (within Forster theory, this object can be considered as an energy acceptor in the absence of a donor) and mutant CK, in which there is no pyocyanine (this object can be considered as donor (allophycocyanin) in the presence of energy acceptor (PS2)) (Fig. 8). Allophycocyanin absorbs light at 550-650 nm and transmits energy to chlorophyll of PS2, and due to this effective excitation cross-section of PS2 fluorescence increases compared with that of the PAL mutant [23].

Analysis of fluorescence induction curves shows that the effective excitation cross-section of PS2 fluorescence increases 1.6-fold after addition of QD 630 (Fig. 7) and 2.6-fold when using allophycocyanin as a light-harvesting antenna (Fig. 8), as compared to the values of effective excitation cross-sections of fluorescence of PS2 lacking additional light harvesters. Therefore, QD is practically not inferior to natural light harvesters in coefficients of acceptor fluorescence growth.

Thus, it is found that quantum dots can form hybrid structures with core complexes of PS2, increasing their absorptive capacity (effective cross section of fluorescence excitation) due to transfer of excitation energy by the inductive resonance mechanism. The data allowed estimation of the coefficient of acceptor fluorescence growth and energy transfer efficiency. It is shown that formation of hybrid structures with QD leads to an increase in the rate of reduction of primary electron acceptors in core complexes of PS2. Clearly, such hybrid systems can be used to increase the light collection efficiency of solar cells based on photosynthesis reaction centers.

This study was partially funded by the Russian Foundation for Basic Research (projects 11-04-01617-a and 11-04-00818-a) and by Ministry of Education and Science of Russian Federation (state contract 16.513.11.3078, Analytic Government Target Program "Development of Scientific Potential of Higher Education", project No. 2.1.1/9396).

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