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Spectral Manifestation of Hybrid Association of $Zn_{0.7}Sd_{0.3}S$ Colloidal Quantum Dots with J-Aggregates of Thiacarbocyanine Dye

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Spectral properties of mixtures of $Zn_{0.7}Sd_{0.3}S$ colloidal quantum dots with mean diameter value of 3.5 nm with the molecules of 3,3′-di(γ-sulfopropil)-9-ethyl-4,5,4′,5′-dibenzo-thiacarbocyanine betaine pyridine salt (DEC), prepared in gelatin were investigated. The obtained data indicated that the formation of well-luminescent *trans*-J-aggregates and spectral tuning in the position of the absorption band of DEC and the luminescence band of quantum dots, providing requirements for resonant energy transfer in the hybrid associate are the determinant factors in the increase of the luminescent emission of DEC molecules, interacting with $Zn_{0.7}Cd_{0.3}S$ colloidal quantum dots.

Keywords: Colloidal quantum dot, J-aggregate, Hybrid associate, Luminescence, Spectrum.

PACS numbers: 78.67.Hc, 81.07.Pr, 81.07.Ta

1. INTRODUCTION

The number of researches devoted to studying of processes of formation hybrid associates of colloidal quantum dots (QDs) with the dye molecules and to research of their spectral properties increases. Their relevance is due to the prospect of using such systems in a number of applications (opto-and nanoelectronics, photocatalysis, biomedicine) [1-7]. Hybrid nanostructures cause a particular interest of researchers owing to the fact that more light-resistant compared to dyes, colloidal quantum dots, are donors of electronic excitation energy [3-5] or electrons [6, 7], which then are used in various photoprocesses. The molecules of the polymethine dyes are perspective to use as acceptors. One of remarkable features of this class of dyes is the ability to formation the ordered J-aggregates [8] which possess unique optical properties.

The problem of formation and degradation of electronic excitations is not completely solved for such systems. So far there are no established views about the interaction between Frenkel excitons, characteristic for J-aggregates, and Wannier-Mott excitons characteristic for QDs. On a way of their decision there is a necessity of an unequivocal establishing of formed hybrid designs.

Techniques of optical spectroscopy are very informative in this respect. They also allow to establish mutual conformity of spectral properties of QDs and J-aggregates, providing conditions for an exchange between them by electronic excitation.

In this paper spectral properties of hybrid associates, formed in the gelatin by direct contact of $Zn_{0.7}Cd_{0.3}S$ open colloidal QDs (mean diameter of 3.5 nm) with molecules of DEC are investigated. Furthermore, associates of CdS QDs having the near mean size with molecules of DEC were prepared for comparison.

2. EXPERIMENTAL SECTION

2.1 Investigated Samples

Colloidal QDs were synthesized by sol-gel method by means of two-jet mixing of aqueous solutions of $CdBr_2$, $ZnBr_2$ and Na_2S in a reactor with a solution of 3 % inert photographic gelatin.

Preparation a mixture of $Zn_{0.7}Cd_{0.3}S$ QDs and CdS QDs with molecules of DEC carried out in the way similar described in [9]. Aqueous solution of DEC of the desired concentration was injected into the heated to 400 C gelatin sol in the final part of the active growth stage of QDs. Such method provided interaction between DEC molecule and growing surface of QDs.

Polycrystals of this substance, high purity of firm Sigma-Aldrich were used for preparation of DEC water solutions. DEC was added in concentrations of 10^{-4}, 10^{-3}, 10^{-2} mole of DEC per 1 mole of QDs (further m.f.). On the average 4-5 DEC molecules are the share of one QD with mean diameter value of 3.2-3.5 nm at the highest concentrations of the used molecules The obtained mixture was applied to glass plates and after that it was dried.

The identification and the certification both of $Zn_{0.7}Cd_{0.3}S$ and CdS colloidal QDs was carried out using a transmission electron microscope LEO ~ 912AB ~ OMEGA. Analysis of the electronic images showed that the obtained QDs have a mean size value of 3.5 nm. Analysis of the reverse electronic dispersion showed that the crystallization of CdS QDs and $Zn_{0.7}Cd_{0.3}S$ QDs occurs in a cubic lattice.

Analysis of the extinction spectra gelatin of layers of CdS QDs and $Zn_{0.7}Cd_{0.3}S$ QDs indicated the presence of dispersed in gelatin open QDs obtained in sol-gel method (Fig. 1). A wide absorption band with feature in the quantum energy range of 3.0-3.3 eV and 3.8-4.0 eV observed for CdS QDs and $Zn_{0.7}Cd_{0.3}S$ QDs, respectively (Fig. 1).

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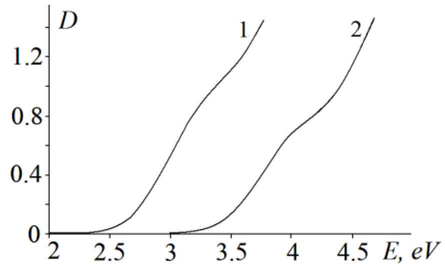

Fig 1 – Absorption spectra of CdS QDs – **1** and $Zn_{0.7}Cd_{0.3}S$ QDs – **2**

Thus, obviously, the observed values of the effective bandgap of the investigated QDs exceed considerably the value of the optical bandgap in the CdS monocrystal with cubic lattice (2.42 eV) and $Zn_{0.7}Cd_{0.3}S$ (3.2 eV), that indicate the manifestation of quantum - size effect.

2.2 Methods of Investigations and Equipment

The investigations were performed with the use of luminescence and absorption techniques.

The absorption spectra of the prepared samples were obtained with the double-beam spectrophotometer Shimatzu-210 UV (Japan). The automatic spectral-luminescence complex was used for measuring of photoluminescence spectra. The sample luminescence was registered with photo-multiplier (R928P Hamamatsu, Japan, energy source battery C4900-51), operating in the photon counting mode and diffraction monochromator MDR-23 (Russia, LOMO). The luminescence of the samples was excited from the region of absorption of QDs by UV radiation was made under excitation by the UV radiation of the diode module HPL-H77GV1BT-V1 ($\lambda_{max} = 380$ nm, $P_{max} = 5$ mW). Moreover, long-wave excitation of luminescence for DEC J –aggregates was performed with the irradiation of laser module KLM-G-635-6-5 ($\lambda_{max} = 635$ nm, $P_{max} = 5$). The results displayed below were obtained at the room temperature (300 K).

3. RESULTS AND DISCUSSION

The absorption and the luminescence properties of associates of DEC molecules and $Zn_{0.7}Cd_{0.3}S$ QDs with various ratios between the components are presented in Fig. 2a, 2b.

The band of J-aggregates located at $\lambda_{max} = 653$ nm was observed in the absorption spectra of DEC and $Zn_{0.7}Cd_{0.3}S$ QDs associate (Fig. 2a). Variation of the concentration value of DEC from 10^{-4} m.f. to 10^{-2} m.f. in the mixture with $Zn_{0.7}Cd_{0.3}S$ QDs was accompanied by nonmonotonic variation of a J-band maximum from 658 nm to 628 nm and 655 nm (Fig. 2a). The band had a complex spectral contour containing a feature at 590-610 nm and narrow peak at 655 nm in the absorption spectrum of DEC concentration value of 10^{-4} m.f. in the presence of $Zn_{0.7}Cd_{0.3}S$ QDs.

The absorption spectra of CdS QDs and $Zn_{0.7}Cd_{0.3}S$ QDs and DEC molecules associates were analyzed taking into account the absorption spectra of gelatin layers of dye. Narrow bands with maxima value of 622 nm to 660 nm appeared in the absorption spectra of DEC in a gelatin matrix for all of the explored concentrations values. These bands are due to the formation of DEC J-aggregates [10, 11]. Most long-wavelength band at 660 nm was observed in the absorption spectrum for maximum concentrations values of 10^{-2} m.f. According to [10] it is related to the absorption of DEC *trans*-J-aggregate, having a close-packed spatial configuration (Fig. 3a). However, the absorption band of J-aggregate shifted monotonously with decreasing of DEC concentration value in short-wavelength region to 635 nm, and then to a band with a maximum at $\lambda_{max} = 622$ nm and a shoulder at 660 nm. According to the authors of [11-13], these bands pertain to the absorption of J-aggregates having more complex structure. In [10] it is proved that the nature of their shortwave shift is due to the *cis*-isomerism. Variation of angle of J-aggregate packing and formation of aggregate of the mixed type constructed from *cis*- and *trans*-dimers is possible, so the nonelementary spectroscopic contour, apparently comprising both of *cis*- and a *trans*-forms of DEC J-aggregates, can observed (Fig. 2c, **3**). Herewith the presence of $Zn_{0.7}Cd_{0.3}S$ shifts this equilibrium toward the all-*trans*-form of DEC J-aggregates (Fig. 2a, **3**).

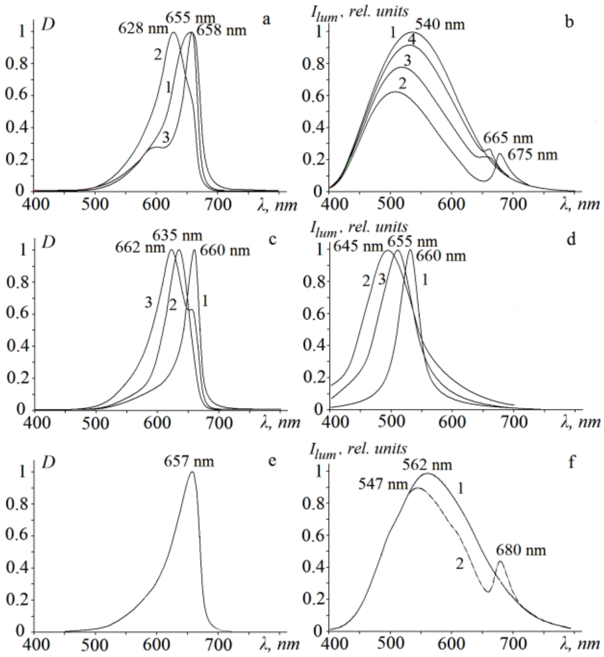

Fig. 2 – Absorption and luminescence spectra of DEC in different environments: (a) absorption spectra of DEC and $Zn_{0.7}Cd_{0.3}S$ QDs associates: $Zn_{0.7}Cd_{0.3}S$ QDs + DEC (10^{-2} m.f.) - **1**; $Zn_{0.7}Cd_{0.3}S$ QDs + DEC (10^{-3} m.f.) - **2**; $Zn_{0.7}Cd_{0.3}S$ QDs + DEC (10^{-4} m.f.) - **3**; (b) luminescence spectra of DEC and $Zn_{0.7}Cd_{0.3}S$ QDs associates: $Zn_{0.7}Cd_{0.3}S$ QDs - **1**; $Zn_{0.7}Cd_{0.3}S$ QDs + DEC (10^{-2} m.f.) - **2**; $Zn_{0.7}Cd_{0.3}S$ QDs + DEC (10^{-3} m.f.) - **3**; $Zn_{0.7}Cd_{0.3}S$ QDs + DEC (10^{-4} m.f.) - **4**; (c) absorption spectra of DEC in gelatin matrix: 10^{-2} m.f. - **1**; $3 \cdot 10^{-4}$ m.f. - **2**; 10^{-4} m.f. - **3**; (d) their luminescence spectra ($\lambda_{exit} = 578$ nm); (e) absorption spectra of DEC and CdS QDs (3.2 nm) associates: CdS QDs + DEC 10^{-2} m.f.; (f) luminescence spectra ($\lambda_{exit} = 380$ nm): CdS QDs (3.2 nm) - **1**; CdS QDs (3.2 nm) + DEC 10^{-2} m.f. - **2**.

The recombination emission band of QDs was observed in the photoluminescence spectrum of the mixtures DEC with $Zn_{0.7}Cd_{0.3}S$ QDs. Its location shifted

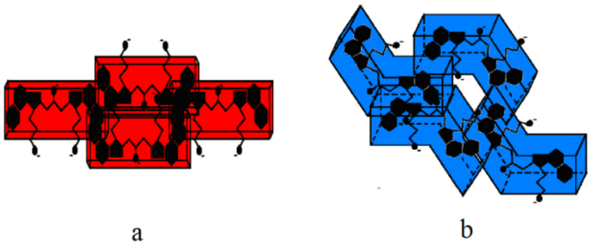

Fig 1 – Structures of *trans*-(a) and *cis*-(b) J-aggregates.

monotonously with increasing of the DEC concentration in the mixture from 540 nm (for DEC molecules absence of gelatin) to short-wavelength region of 500 nm (Fig. 2b, **1**-**4**). This feature is probably due to the effect of reabsorption of QDs emission by DEC J-aggregates.

Moreover, there was a feature in the luminescence spectrum of QDs at a DEC concentration value of 10^{-4} m.f. which increased monotonically with increasing of J-aggregates concentration value, and the dip was observed in the absorption region of associated DEC J-aggregates at maximum concentration value of dye (10^{-2} m.f.), and luminescence of DEC J aggregates was observed in the spectral range 665 nm-675 nm. The resonance energy transfer of electronic excitation from $Zn_{0.7}Cd_{0.3}S$ QDs to the J-aggregate may be the reason of changing the shape of the luminescence band. The presence of a dip in the area matched to a maximum of J-aggregate emission is explained by the Fano theory [14].

Another important detected feature is non-monotonic behavior of the luminescence intensity of DEC J-aggregates in the mixture with $Zn_{0.7}Cd_{0.3}S$ QDs. The weakest luminescence of associated DEC J-aggregates was observed at a concentration value of 10^{-3} m.f. and emission intensity of J-aggregates was greater for concentration value of 10^{-4} m.f., despite the fact that the absorption was less. This behaviour becomes clear if to consider that *cis*-J-aggregates forms mainly for concentration value of 10^{-3} m.f. (Fig. 2c, **2**). In turn, it is considered that J-aggregate constructed from the *trans*-form is more rigid and luminesces greater in compared with J-aggregate of the *cis*-form as DEC *trans*-form is more symmetrical.

4. CONCLUSIONS

Thus, comparison the spectral data of mixtures of DEC molecules with $Zn_{0.7}Cd_{0.3}S$ QDs with the corresponding the spectral data of DEC J-aggregates in gelatin matrix suggested a hybrid association of DEC J-aggregates and $Zn_{0.7}Cd_{0.3}S$ QDs. Formation of DEC *trans*-J-aggregates contributes significantly in the observed luminescence properties of the hybrid associates.

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