Formation of J-aggregates of Thiamonomethincyanine Dyes in the Presence of CdTe Nanoparticles.

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The conditions of formation of J-aggregates for three types of thiamonomethincyanine dyes, whose structure is differed by end groups, are studied depending on their concentration and type of interaction with CdTe nanoparticles with size of about 3 nm in aqueous dispersions. The influence of dye structure on the efficiency of formation of J-aggregates in solutions and in films was found. It was found that quantum dots (QDs) of CdTe stabilized by thioglycolic acid can adsorb J-aggregates of the dye molecules on their surface. It was shown for the first time that the hybrid structure of dye-CdTe can be formed through the interaction of negatively charged dye molecules and negatively charged surface of the QDs through the formation of neutral aggregates. It was not found any processes of energy transfer from dye to the particles of CdTe neither for the dimer - CdTe system nor for the J-aggregates – CdTe system.

Keywords: J-aggregates, Nanocrystals of CdTe, Composite Films, Hybrid Aggregates, Monomers, Dimers.

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1. INTRODUCTION

In the recent years a growing interest has been paid to the ability of organic dyes to self-organization in the presence of nanoscale additives in solutions. For example, the influence of clay impurities in a solution on spectral characteristics of pseudoisocyanine (PIC) was shown in ref. [1]. The authors of this work showed easy formation of J-aggregates under these conditions as well as their high stability. Also, research was conducted on influence of fine particles such as CdSe on J-aggregation of organic dyes. In ref. [2] it was considered the formation of compounds of J-aggregates with quantum dots, which have been obtained by a combination of positively or negatively charged aggregates of dyes and oppositely charged quantum dots. This effect is caused by electrostatic attraction between dye molecules and nanocrystals.

On the other hand, the interaction between equally charged particles has not been studied because of expected electrostatic repulsion and the inability to associate into a hybrid aggregate. In this work, we made an attempt to get J-aggregation of selected dyes on quantum dots of CdTe, whose surface has the same sign of charge as the dye molecule itself.

2. EXPERIMENTAL PART

2.1 Samples preparation

CdTe dispersion in water was obtained by the method described in ref. [3]. Shortly, the synthesis was carried out through interaction of CdI_2 and H_2Te induced by electrochemical reduction of tellurium on tellurium electrode in the presence of thioglycolic acid (TGA). After centrifugation, the resulting solution has been obtained which contained nanocrystals with the narrow size distribution.

The diameter of CdTe nanoparticles was determined from the ratio of particles size and the absorption wavelength of the first exciton peak [4].
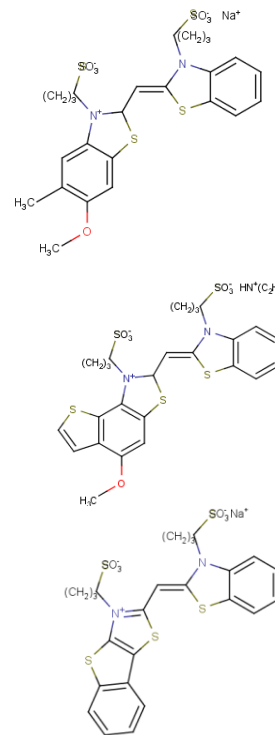

Fig. 1 – Chemical structure of dyes

From these data $D = 3$ nm, the concentration of CdTe $c = 8.5 \times 10^{-6}$M.

Aqueous mixtures of dyes and nanoparticles were prepared as follows: first, the stock dye solution was added to the cuvette with water and then colloidal nanocrystals of CdTe were added to the resulting solution. To compare the behavior of the solutions a dispersion of CdTe in the same cuvette was prepared separately.

Composite films were prepared from the final solutions which were done by solution casting on glass plates using the dispenser.

2.2 Methods of investigation

To measure the absorption spectra and photoluminescence used spectrophotometer Avantes-2048, as the source of excitation for the measurement of luminescence spectra used laser with a length of emitted light 408 nm and to measure the absorption spectra used halogen lamp Ocean Optics LS-1.

Investigation of the morphology of films was carried out in polarized and neutral light on biological microscope of research class XY-B2. When considering samples in polarized light polarizer was set between the light source and sample and analyzer on oculars.

3. RESULTS AND DISCUSSION

3.1 Spectral manifestations of aggregation of dyes in aqueous solutions

With increasing concentration of dye in aqueous solutions it was found that the dyes form compounds of two types. First, the monomer absorption band at ∼ 435 nm in dilute solution gradually turns into a shortwave band at ∼ 415 nm, indicating the formation of dimers of the dye (Fig. 2). A similar pattern was found for dyes 2 and 3, but from their absorption spectra it can be concluded that molecules of 2 form dimers in water not so effective as compared to 1 and 3.

Second, a further increase of dye concentration leads to decreasing molar extinction coefficient and broadening of the absorption band, indicating the formation of larger aggregates than dimers (Fig. 2, curves 5, 6). On the other hand, it was not observed clearly an expressed manifestation of J-aggregation of dyes in the absorption spectra of aqueous solutions.
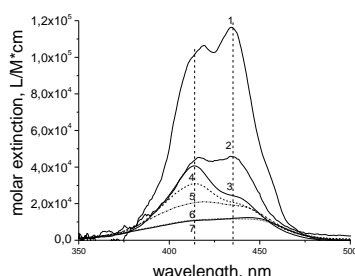

Fig. 2 – molar extinction of dye 1, presented at different concentrations of the dye: **1**-concentration $4 \cdot 10^{-7}$ M; **2**- $9,1 \cdot 10^{-7}$ M; **3**- 10^{-5} M; **4**- $3,15 \cdot 10^{-5}$ M; **5**- $6,21 \cdot 10^{-5}$ M; **6**- 10^{-3} M in the cuvette of 1 mm thickness; **7**- $1,09 \cdot 10^{-4}$ M in the cuvette of 1 cm thickness, the solvent was water

3.2 Interaction of CdTe nanocrystals with dyes in the electrolyte solution

Dissolution of dyes in the electrolyte leads to a narrow absorption band shifted relative to the absorption of monomers to the red side of the spectrum at wavelength $\lambda = 471$ nm (for dye 1, Fig. 3) that testifies formation of J-aggregates. It was found that the addition of dispersion of CdTe into the dye solution in the electrolyte may affect its structure, which in turn depends from the structure of the dye itself. Thus, the addition of dispersion of CdTe to the solution of dye 1 showed no significant change in absorption spectra.

Fig. 3a shows that the absorption spectra of CdTe with the dye are almost superposition of spectra of individual components of the solution, from these data one cannot conclude about the influence of CdTe on the dye. But in the photoluminescence spectra of dye in the presence of CdTe an increase in J-aggregate photoluminescence intensity was observed (curve 4, Fig. 3b).

The difference in the changes in photoluminescence and absorption spectra can be explained by the fact that the quantum yield of luminescence of J-aggregates are much larger compared to the quantum yield of luminescence of dye monomers, while the extinction coefficients of monomers and J-aggregates are very close (Fig. 4), so effects of J-aggregate restructuring are better seen in the spectra of luminescence, but almost invisible in the absorption spectra.

Thus we can note a tendency of increasing the number of J-aggregates under the action of CdTe. But, similar to the case of monomers, the interaction of J-aggregates and CdTe does not lead to the effect of energy transfer.

Reshape of the band in the luminescence and absorption spectra of the dye by adding nanocrystals provides additional evidence that the dye molecules interact with nanoparticles. The same electric charge of components (dye and nanocrystals of CdTe) indicates that the interaction should result in electrostatic repulsion. In our view, however, the formation of neutral J-aggregates by use of ions of electrolyte is a critical condition for the interaction. Neutral unit is capable to be adsorbed on the surface of the nanocrystal, thus the equilibrium changes in solution between free molecules and those bounded with the nanoparticles. Removal of aggregates from the solution by nanoparticles leads to the emergence of new J-aggregates from monomers and dimers in the solution, which are adsorbed on the surface of CdTe. Hybrid particles of CdTe/J-aggregate are insoluble and precipitate. Further evidence of the specific formation of the composite material follows from the film structure.

3.3 Formation of composite films

Deposition of dye molecules from solution in the form of a film naturally leads to their association and the formation of aggregates. Even in films formed from the aqueous solution J-aggregation of molecules takes place. Most clearly this is evident in the film of dye 3 (Fig. 5a), where the units form a chain-like structure.

The chain could be observed by using of polarization microscopy (Fig. 5b), which means that this structure rotates the angle of polarization which is attributed to the crystalline structure. The absorption spectra of film of dye 3 (Fig. 6) shows a narrow band with maximum at 487 nm, inherent to J-aggregates, which confirms that the film is composed mainly of J-aggregates. On the other hand, the morphology of films of dyes 1 and 2 formed from aqueous solutions and their absorption spectra (Fig. 6) shows a less clear trend to the formation of J-aggregates.
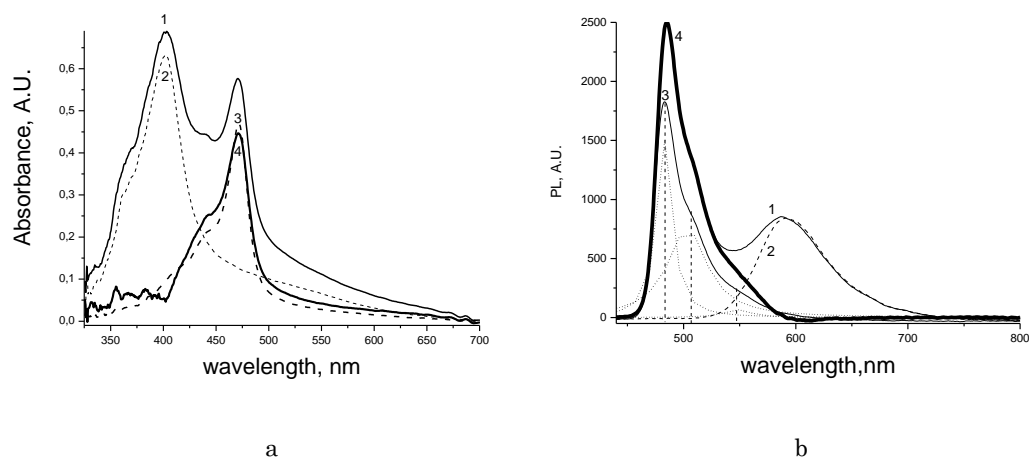
a

b

Fig. 3 – Spectra of (a) absorption and (b) photoluminescence upon addition of dispersion of CdTe to the solution of dye 1 in the electrolyte: **1**- a mixture of CdTe $(2,6 \cdot 10^{-6}M)$ and dye $(10^{-4}M)$; **2**- CdTe $(2,6 \cdot 10^{-6}M)$ in the absence of dye; **3**- dye $(10^{-4}M)$ in the absence of CdTe; 4- the difference of spectra 1 and 2. Thickness of cuvette is 1 mm
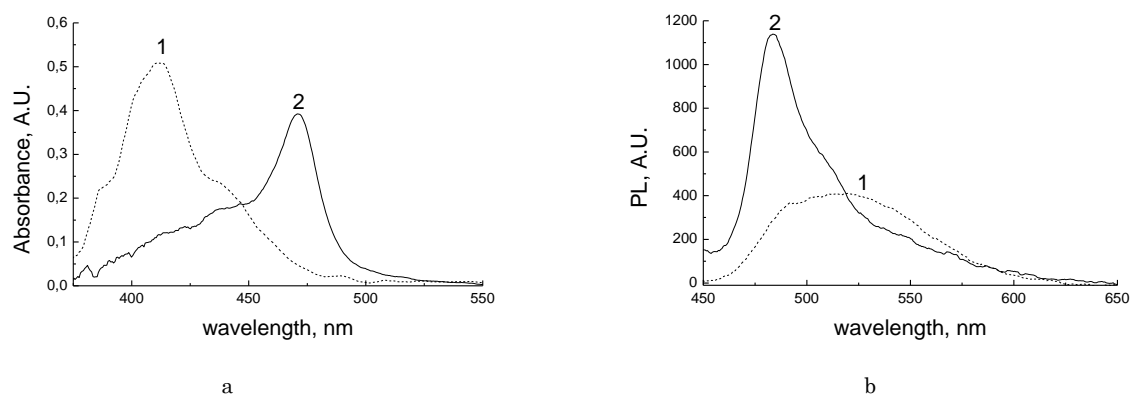

a

b

Fig. 4 – Spectra of (a) absorption and (b) photoluminescence of dye 1 with concentration of ca. $10^{-4}M$ in aqueous solution (1) and in aqueous solution of KCl electrolyte with concentration of ~ 0.1M (2). Thickness of the cuvette is 1 mm

By comparing Fig. 5a and Fig. 5c, we see a significant difference between the morphology of films: CdTe nanocrystals mixed with dye 3 form a woody-like structure. A similar morphology was observed for hybrid films based on two other dyes. To clarify the mechanism of formation of those structures it has been made a calculation of fractal dimensions for structures shown in Fig. 5c. Fractal dimension was calculated by the method described in [5]. The image was broken into a grid of cells, each of them was attributed to filled or empty volume, and the number of the filled cells was calculated.
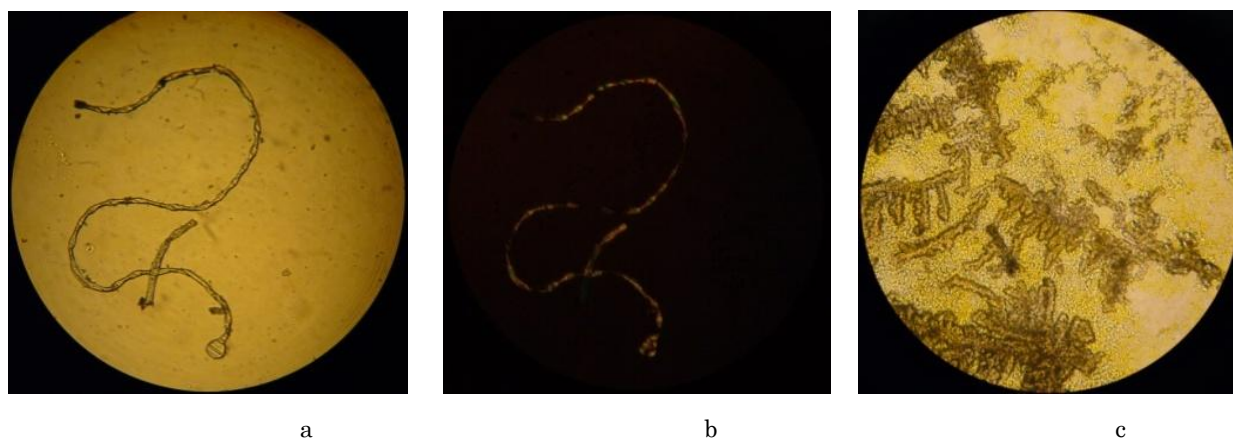

a

b

c

Fig. 5 – Image of (a), (b) the film of dye 3 from an aqueous solution and (c) hybrid film of dye 3 - CdTe nanocrystals from an electrolyte solution, magnification is $\Gamma = 200$. (a), (c) images obtained with non-polarized light and (b) with crossed polarizers
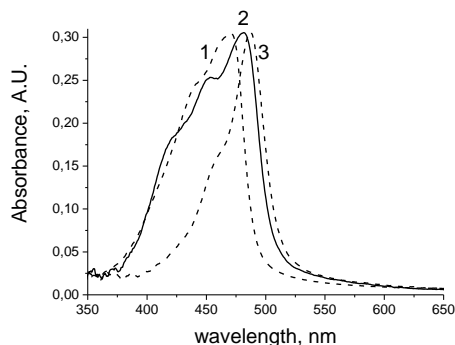
Fig. 6 – The absorption spectra of films formed from dyes 1, 2 and 3, respectively, obtained from their aqueous solutions

From this value we obtain a fractal dimension D:

$$D = \frac{\ln N_1}{\ln(L / l_0)}$$

where N_1 is the number of the filled cells, L is the size of the image, l_0 is cell size.

For dye 2 it was obtained $D \approx 1{,}76$ and for dye 3 $D \approx 1{,}74$. According to [6], these values correspond to the model of cluster-cluster aggregation (CCA). It means that the clusters from initial particles are formed first followed by their further ripening together. This model is consistent with the conclusion that the adsorption of J-aggregates on the surface of the CdTe nanoparticles takes place, resulting in hybrid clusters that precipitate in the form of a fractal structure.

4. CONCLUSIONS

Based on the research of behavior of three types of thiamonometyncyanine dyes in aqueous solution, electrolyte solution and in films it was found the different ability to form J-aggregates depending on the dye structure. The absence of end groups near phenolic ring in the molecule of dye 3 leads to a more clearly expressed formation of J-aggregates in the films. But two other dyes showed better ability to form J-aggregates in electrolyte solutions. The formation of J-aggregates for all types of molecules proceeds through formation of dimers as an intermediate step.

The dyes also showed different ability of interaction with CdTe nanocrystals. In aqueous solutions, where the formation of J-aggregates are very slow, the forces of electrostatic repulsion of equally charged dye molecules and particles of CdTe do not allow for the formation of any hybrid structures. In the electrolyte solution, neutral J-aggregates can be adsorbed on the surface of CdTe and thus form a hybrid structure that precipitates. Shift of equilibrium in the solution due to separation of hybrid particles leads to further formation of J-aggregates from free molecules in the solution. Dye 3 showed the most effective process of the formation of J-aggregates in the presence of CdTe particles. Thus, the presence of end groups near phenolic rings of thiamonomethincyanine molecule is a critical condition for the formation of J-aggregates both in the presence and in the absence of the inorganic particles.

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