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## INFLUENCE OF CdSe NANOPARTICLES ON STABILITY OF POLYMETHINE DYES IN WATER

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*We present the results of studies of the influence of CdSe nanoparticles on the color stability of polymethine dyes. Two structurally similar dyes with different abilities to form J-aggregates in water were considered. We have observed a significant increase in the color stability of dyes, as a result of the interaction with 1.1-, 1.2-, and 2.3-nm nanoparticles.*

*Keywords:* semiconductor nanoparticles, polymethine dyes, J-aggregates, optical absorption.

### 1. Introduction

Such objects of investigation as the complexes formed from polymethine dyes (PMD) and nanoparticles (NP) attract more and more attention of researchers. The ability of many species of PMD to the formation of aggregates is an important property for their applications. There are a lot of papers devoted to the influence of the environment on the formation of aggregates (see, e.g., [1, 2]). The formation of J-aggregates in a solution of reverse micelles was considered in [1], and the authors of work [2] studies the influence of multiply charged inorganic and organic cations on the J-aggregation of polymethine dyes. In spite of a fast growing number of publications devoted to the binding of dye molecules to semiconductor and metallic nanoparticles (NPs), there are still a lot of questions about the interaction between them [3, 4, 7, 8]. Such questions about the influence of adsorption and aggregation of dye molecules on the surface of nanoparticles on the light absorption, decay of excited states, and the photoinduced degra-

ation of dye molecules are still remains unstudied. It is known from the literature [3] that NPs usually contribute to the formation of J-aggregates. But another situation is possible as well. The authors of work [4] showed that it is possible that all dye molecules are bound to NPs. As a result, the process of aggregation would be impossible at some concentrations of NPs and a dye. Semiconductor nanoparticles of the A<sub>II</sub>B<sub>VI</sub> group are important objects for studying due to the large area of their possible practical applications [5]. The possibility to obtain the low-toxicity nanoparticles possessing the luminescent properties makes them perspective objects for the application to biological investigations [6]. The combination of polymethine dye molecules and semiconductor nanoparticles can lead to a significant improvement of their properties. In works [7, 8], the formation of systems with resonant energy transfer that include semiconductor nanoparticles and J-aggregates was studied.

In this work, we will present the experimental results of our study of the interaction between CdSe nanoparticles and PMD molecules. In Section 2, the experimental details are described. Experimental results and the discussion are shown in Section 3.

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## 2. Experimental Details

We used three different types of CdSe nanoparticles: 1.2-nm NPs with narrow size distribution (NP1) and 1.1- and 2.3-nm NPs with wide size distribution (NP2 and NP3, respectively). For 1.2 nm NPs with narrow size distribution, we used the method of growing of the so-called magic clusters in aqueous solution, as described in [9]. In our work, we took CdCO<sub>3</sub> as a Cd precursor which led to a considerable reduction of the reaction time (down to 15 min).

NP1 1.2-nm magic clusters with narrow size distribution were obtained by the following method: we mixed 0.75 ml of 0.05 M Na<sub>2</sub>SeSO<sub>3</sub> with 2 mg of CdCO<sub>3</sub> in 9.25 ml distilled water, then 15 mg NaOH and 16 mg of L-cysteine were added. The growth of nanoparticles occurred with a constant stirring for 15 min and the storage during one day in a dark room at a temperature of 20–25 °C.

NP2 crystalline-like 1.1-nm nanoparticles with wide size distribution were obtained by the nonselective photoetching of NP1 by a 406-nm semiconductor laser during 26 min at room temperature and a constant stirring. This led to the removal of some atoms from the surface. At that time, we observed the formation of a white sediment of cadmium hydroxide.

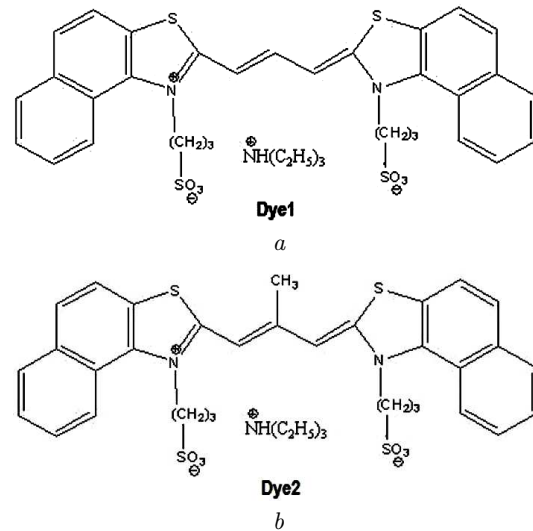
NP3 were obtained in the following way: 2 ml of 0.05 M Na<sub>2</sub>SeSO<sub>3</sub> were mixed with 18 mg of CdCO<sub>3</sub> in 10 ml distilled water, then 16 mg NaOH and 40 mg of L cysteine were added. The growth of nanoparticles occurred with a constant stirring for 15 min and the storage during one day in a dark room at a temperature of 20–25 °C.

The size of nanoparticles was estimated by the provisions of the maxima of their absorption spectra, according to formula (1), which was taken from [10]. The maxima of the absorption bands of NP1, NP2, and NP3 stay at wavelengths of 420, 408, and 510 nm, respectively. According to work [10], it corresponds to 1.22-, 1.1-, and 2.3-nm nanoparticles.

$$D[\text{nm}] = 0.334 \exp\left(\frac{(\lambda_{\text{max}}[\text{nm}] - 252.7)}{129.3}\right). \quad (1)$$

In this paper, we use two structurally similar dyes (see Fig. 1). Dye1 forms no aggregates in water solutions, and dye2 is able to form J-aggregates. The dyes were obtained by the standard method in accordance with [11].

A grating monochromator MDR-3 was used for the recording of absorption spectra. A halogen incandes-



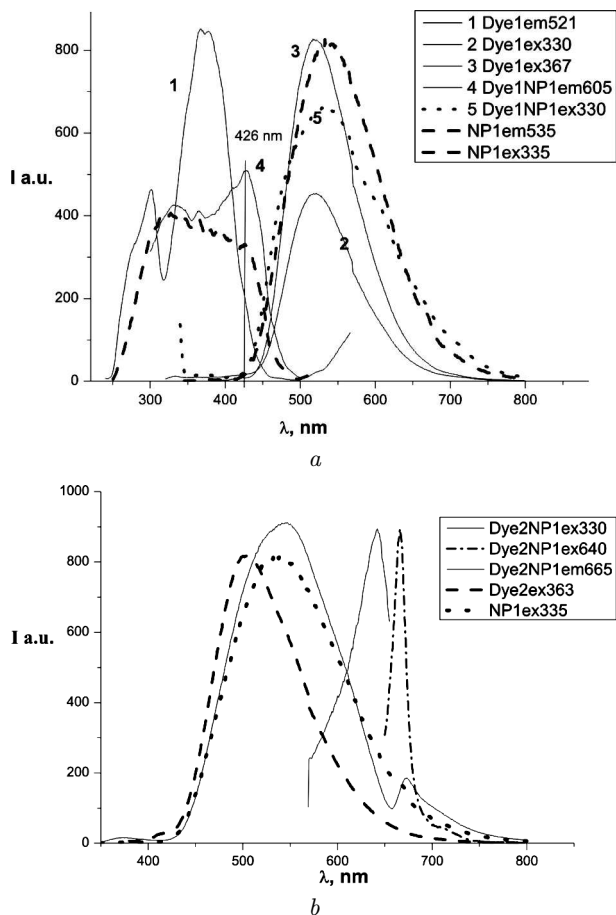
**Fig. 1.** Structural formulas of polymethine dyes. Dye1 (a) does not form aggregates in water solutions, Dye2 (b) is able to form J-aggregates

cent lamp was used as a light source for absorption spectra. Photoluminescence (PL) spectra were obtained, by using a Cary Eclipse spectrophotometer (Varian, Australia).

## 3. Results and Discussion

### 3.1. Photoluminescence of polymethine dyes conjugated with 1.2-nm CdSe nanoparticles

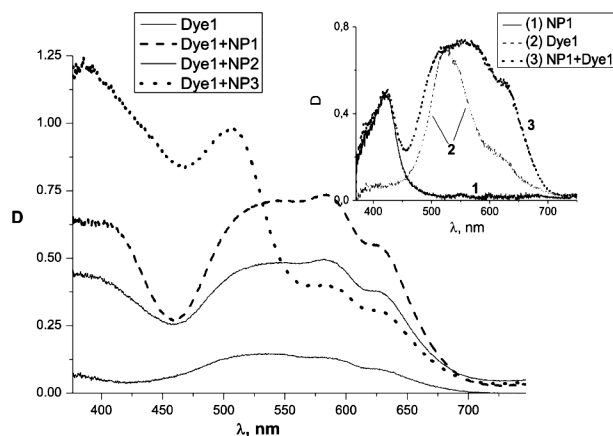
The PL and excitation spectra of dye1 and dye1 bound to 1.2-nm NPs are shown in Fig. 2, a. Comparing the PL spectra of free dye1 and dye1 bound to NP (curves 2, 3 and 5), we could see the broadening of the emission contour in the presence of NPs. It can be related to the overlapping of emission bands of the dye and nanoparticles and to a transformation of the emission spectrum of dye molecules in the presence of NPs, since it was observed that the absorption spectrum of the dye undergoes changes in the presence of NPs. In that case, an enhancement of side bands in the absorption spectrum of the dye was observed (see the inset in Fig. 3). The excitation spectrum of that sample shows that the emission near 605 nm is related to nanoparticles, since the excitation spectrum matches the excitation spectrum of nanoparticles (Fig. 2, a). As a result of the possibility to form aggregates in the case of dye2, there was a quite other picture. The formation of J-aggregates of dye2 in an aqueous solution at a concentration of



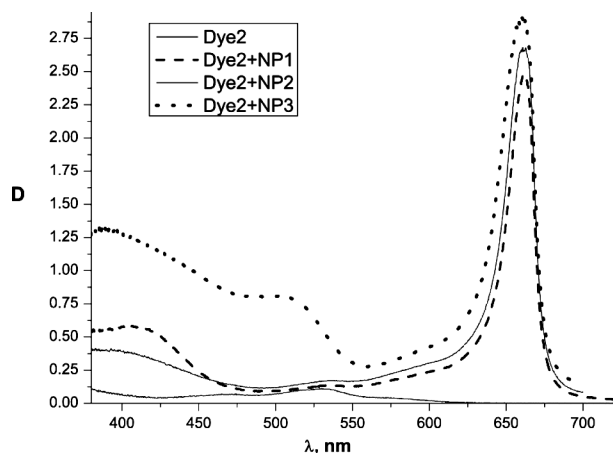
**Fig. 2.** PL spectra of PMDs with 1.2-nm nanoparticles. Dye1 spectra are shown in (a). Curve 1 shows the excitation spectrum; curves 2, 3 present the luminescence spectra of dye1, curves 4 and 5 are the excitation and emission spectra of NP + dye1; and dashed lines correspond to just NPs. Dye2 spectra are shown in (b). Dashed curve shows the luminescence spectra of dye2, dotted curve – NPs, and solid curve – NP + dye2. The band at 665 nm corresponds to PL of J-aggregates of dye2. Excitation spectrum of J-aggregates is shown by the solid curve with the maximum at 640 nm. Dot-dashed line shows the PL spectrum of J-aggregates bound to NPs under 640-nm light excitation

$1 \times 10^{-5}$  M, which was used, does not occur usually. But, as a result of the electrostatic attraction of polar dye molecules to nanoparticles, there is a local increase of the dye concentration in vicinities of NPs. Therefore, the aggregates are formed [3]. This was observed for all nanoparticles used in the work (Fig. 4). So, the PL of dye2 + NPs consists of the emission band of nanoparticles and the slight band at

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**Fig. 3.** Absorption spectra of dye1 and dye1 bound to nanoparticles with diameters of 1.2, 1.1, and 2.3 nm; 2 weeks after the preparation. The inset shows the absorption spectra of 1.2-nm nanoparticles (curve 1), dye1 (curve 2), and the dye with NP (curve 3), just after the preparation



**Fig. 4.** Absorption spectra of dye2 and dye2 bound to nanoparticles with diameters of 1.2, 1.1, and 2.3 nm; 2 weeks after the preparation

670 nm that corresponds to the PL of J-aggregates of dye2 (Fig. 2, b).

### 3.2. Influence of CdSe nanoparticles on the color stability of polymethine dyes

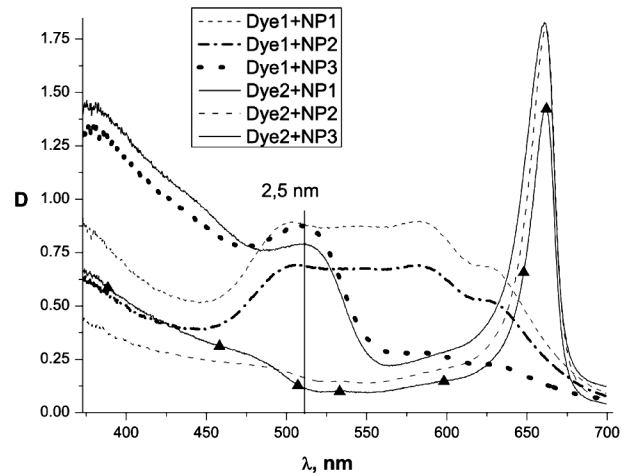
In this section, we present the results of studies of the influence of CdSe nanoparticles on the color stability of PMDs in water solutions. The optical density of dyes, used in this work, decreases more than twice (in dark room) and by five times for two weeks (from 0.74 to 0.15 for the solution with a dye concentra-

tion of  $1 \times 10^{-5}$  M). The presence of CdSe nanoparticles leads to a significant increase of studied dyes' color stability. As is shown in Figs. 3 and 4, the situations in the cases of dye2 that forms J-aggregates and dye1 that does not would be completely different. For colloidal solutions of dye1 conjugated with NPs, it turned out after two weeks of the storage that the highest value of optical density in the region 500–650 nm, which corresponds to dyes' absorption bands, was in the case of the binding of PMD molecules to 1.2-nm NP1. In the case of 1.1 nm crystalline-like NP2, the value of optical density was smaller; and it was smallest for 2.3-nm NP3. It should be noted that, in the last case, the absorption band of PMD at 520 nm was overlapped by the NP3 absorption band at 505 nm. The absorption spectra of dye1, NP1, and dye1 conjugated with NP1 just after the mixing are shown in the inset in Fig. 3. It is well seen that the presence of nanoparticles leads to an increase of the PMD absorption side bands.

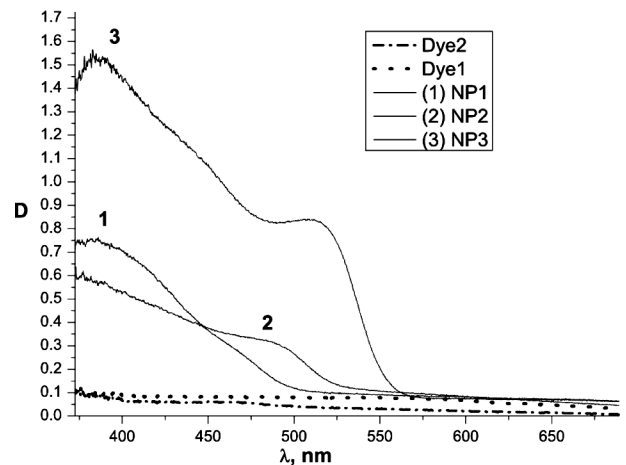
In the case of Dye2 that is able to form J-aggregates in water, all will be entirely different. In the presence of NP, the dye molecules in a solution would be mostly in the aggregated state, because the presence of nanoparticles leads to a local increase of the PMD concentration in the solution just around nanoparticles and thus contributes to the formation of dye aggregates. The largest value of optical density corresponds to the solution with the largest nanoparticles. For the solution of PMD conjugated with fullerene-like NPs (NP1), the absorption band of J-aggregates is smallest.

The absorption spectra of these solutions after the 4-month storage (in dark, at room temperature) are shown in Fig. 5, and the spectra of nanoparticles and dyes separately are shown in Fig. 6. As is seen from Fig. 6, both dyes in the absence of NPs are almost completely decolorized. By comparing Figs. 3 and 5, we can see that the value of optical density of the solutions of dye1 mixed with 1.1-nm and 1.2-nm NPs stayed fairly constant, whereas the optical density of the solution dye1+NP3 (2.3 nm) was decreased by half. The absorption band of J-aggregates of dye2 was decreased too. This can be related to the degradation of PMD or to a gradual precipitation of NPs with bound dye molecules and the subsequent sedimentation.

Comparing Figs. 5 and 6, we can see that different changes are could be observed also for the solutions



**Fig. 5.** Absorption spectra of dyes 1 and 2 conjugated with nanoparticles with diameters of 1.2, 1.1, and 2.3 nm; 4 months after the preparation



**Fig. 6.** Absorption spectra of dyes 1 and 2 and colloidal solutions of nanoparticles with diameters 1.2 (curve 1), 1.1 (curve 2), and 2.3 nm (curve 3); 4 months after preparation

of pure NPs and the solutions of NPs in the presence of dyes. It could be seen that, in the case of 1.1-nm nanoparticles, there were certain transformations of the absorption spectra, namely a broadening of the absorption band with the simultaneous appearance of a long-wavelength maximum and a simultaneous reduction of the value of optical absorption. This can be explained by the process of Ostwald ripening. For nonphotoetched 1.2-nm nanoparticles, this process goes much slower (Fig. 5). Apart from that, this process goes slower in the presence of the dyes in a solution for both types of NPs (1.2-nm magic clusters

and 1.1-nm crystalline-like nanoparticles). NP3 were grown from 2.3 nm to 2.5 nm, and the presence of PMD had no considerable effect.

#### 4. Conclusions

It is shown that the discoloration of the studied PMD solutions is going much slower in the presence of cadmium selenide nanoparticles. The dye able to form aggregates in water solutions is mainly in the aggregated form. We have found that the discoloration process of the dye conjugated to CdSe nanoparticles depends on NP's size and structure. Moreover, the optimal size of nanoparticles will be different for the dye, which is in the molecular form, and the dye in the form of aggregates.

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#### ВПЛИВ CdSe НАНОЧАСТИНОК НА СТАБІЛЬНІСТЬ ПОЛІМЕТИНОВИХ БАРВНИКІВ У ВОДІ

#### Резюме

Наведено результати дослідження впливу наночастинок селеніду кадмію на стабільність кольору поліметинових барвників. Розглянуто два структурно близькі барвники із різною здатністю до утворення J-агрегатів у воді. Внаслідок взаємодії барвників із наночастинами розміром 1,1, 1,2 та 2,3 нм спостерігалось значне підвищення стабільності кольору розчинів, що досліджувалися.