

Luminescence photomodulation of nanospheres with CdSe/ZnS quantum dots in polymer films

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The results of studies of the spectral-kinetic (absorption and fluorescent) characteristics of the polymer nanospheres created by us (containing luminescent inorganic CdSe/ZnS quantum dots and photochromic diarylethene molecules) incorporated into a polymer film are presented. A reversible modulation of the fluorescence intensity of quantum dots, caused by the photoisomerization of diarylethene molecules, was found. It is shown that nanospheres in polymer matrices exhibit higher efficiencies of both photoinduced modulation of QD radiation and Förster resonance energy transfer (FRET) from QDs to the cyclic isomer of DAE as compared to solutions. The results can be used, for example, to create luminescent photocontrolled panels based on films containing fluorescent nanoparticles.

Keywords: photochromism, fluorescence, quantum dot, Förster resonance energy transfer, polymer nanospheres, polymer films

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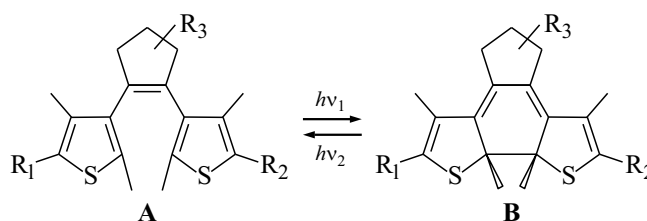
Introduction

In recent years, a new direction in the field of photochromism has been developed — the development of photochromic fluorescence nanomodulators, which are „core–shell“ systems [1]. As a core, nanocrystals of inorganic semiconductors of various types are used — quantum dots (QDs) emitting in the visible region of the spectrum. Their practical significance is due to the fact that they have a wide spectral region of excitation and a narrow fluorescence band, high luminosity and photostability.

To create a shell, molecules of photochromic compounds of various structures are used, which are adsorbed on the surface of QD [2–7]. Photochromic transformations of these compounds, which exhibit photoinduced absorption in the QD radiation region, provide reversible photoinduced modulation of the QD fluorescence intensity due to both inductive resonance energy transfer from QD to the colored isomer of the photochromic molecule (FRET) [8–10] and QD radiation reabsorption with the same colored isomer.

Photochromic compounds from the class of thermally irreversible diarylethenes (DAE) [11], in which photochromic transformations between A and B isomers occur only under

the action of radiation absorbed by them, without dark relaxation (Scheme 1), are of the greatest practical interest for the development of photochromic nanomodulators of QD radiation.



Scheme 1.

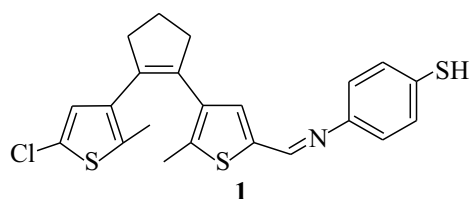
Open colorless DAE (A) isomer, absorbing UV radiation, is transformed to a colored (cyclic) DAE (B) isomer, which, under the action of visible radiation absorbed by it, again turns into the initial open isomer.

This article continues our previous studies on the creation of nanophotoswitches based on CdSe/ZnS QDs and photochromic compounds from the DAE class [12–15]. The purpose of the study was to study the spectral (absorption and fluorescence) properties of polymer nanospheres containing QDs and DAE in polymer films, in comparison with

the results obtained earlier for such polymer nanospheres in solutions [15].

Experimental part

The objects of study were polymer films specially created for this work, including polymer nanospheres (synthesized by the [15] method) containing QDs and photochromic DAE **1** (Scheme 2). The optical characteristics of the objects were controlled by spectrophotometry and fluorescence spectroscopy.



Scheme 2.

CdSe/ZnS QDs were synthesized at the Research Institute for Physical Chemical Problems of the Belarusian State University in accordance with an adapted protocol. Polymer nanospheres were obtained by encapsulating and solubilizing CdSe/ZnS QDs in water by introducing DAE **1** molecules into a thin polymer shell over hydrophobic QDs according to a published procedure [16].

For embedding into polymer films, a 10% solution of polyvinyl alcohol (PVA) was added to the synthesized nanospheres. After thorough mixing, the mixture was applied to a lavsan substrate and dried.

Spectral-kinetic studies of photochromic transformations of DAE in solutions and in polymer films were carried out using SPECORD 200 (Carl Zeiss, Germany) and Cary 50 Bio (Varian, Australia) spectrophotometers, as well as LC-4 lamps (Hamamatsu, Japan). The samples were irradiated with UV light through a UFS-1 light filter, and with visible light through a ZhS-16 light filter. The irradiation time required to transfer DAE between forms A and B was determined based on the absorption spectra measured in the equilibrium state.

Fluorescence spectra were recorded using SM2203 (Solar, Belarus) and Cary Eclipse (Varian, Australia) spectrofluorimeters.

Results and discussion

Based on the results obtained earlier [14], it is known that the absorption band of the photoisomerized cyclic form of DAE **1** is located in the range of 450–600 nm and (unlike the spectrum of the initial open form) overlaps with the QD emission band. This makes it possible to use such QDs as potential FRET donors, and molecules of the photoisomerized form of DAE **1** as FRET acceptors.

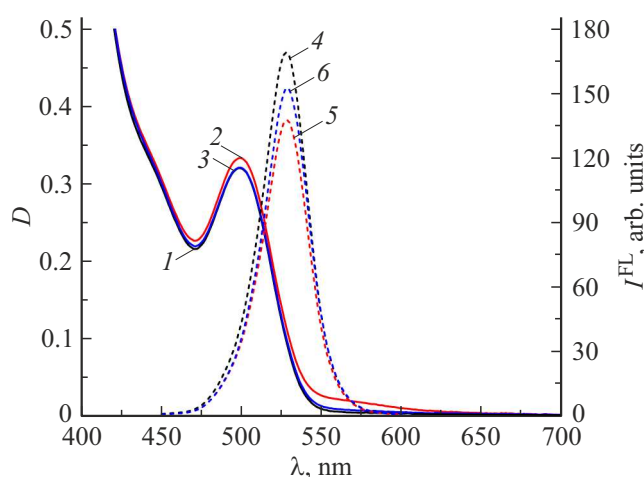


Figure 1. Absorption (curves 1–3) and fluorescence spectra upon excitation at wavelength of 440 nm (4–6) of QD in toluene in the presence of DAE **1** before UV irradiation (1, 4), after UV irradiation (2, 5), after subsequent visible light irradiation (3, 6) [14].

Based on these spectral data, the Förster critical radius $R_0 = 4.7$ nm [14] was calculated. The Förster radius R_0 (in Å) was estimated according to the expression

$$R_0 = 0.211(\kappa^2 n^{-4} Q_D J(\lambda))^{1/6}, \quad (1)$$

where κ^2 — a factor describing the mutual spatial orientation of the dipole moments of the donor and acceptor transitions, n — the refractive index of the medium, Q_D — the quantum yield of the donor in the acceptor absence, $J(\lambda)$ — overlap integral reflecting the degree of spectral overlap between the emission of a donor and the absorption of an acceptor,

$$J(\lambda) = \int_0^{\infty} F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda, \quad (2)$$

$F_D(\lambda)$ — normalized donor fluorescence intensity, $\varepsilon_A(\lambda)$ — acceptor extinction coefficient.

The absorption and fluorescence spectra of QD525 (with an emission band maximum of about 525 nm) in toluene in the presence of DAE **1** before and after irradiation with activating UV radiation are shown in Fig. 1.

Photoinduced spectral changes in toluene solution containing QD525 and DAE **1** molecules (Fig. 1) are similar to those observed for a DAE **1** solution in the absence of QD [14]. However, the absorption band of the photoinduced cyclic form shifts bathochromically by 20 nm, which indicates the chemical interaction of DAE **1** with the surface of QDs. As can be seen from Fig. 1, after UV irradiation, which leads to formation of cyclic colored form B of DAE **1** molecules in solution, the fluorescence intensity of QDs decreases, and subsequent irradiation with visible light, which restores the open colorless form A of DAE **1**, leads to an increase in the QD fluorescence intensity.

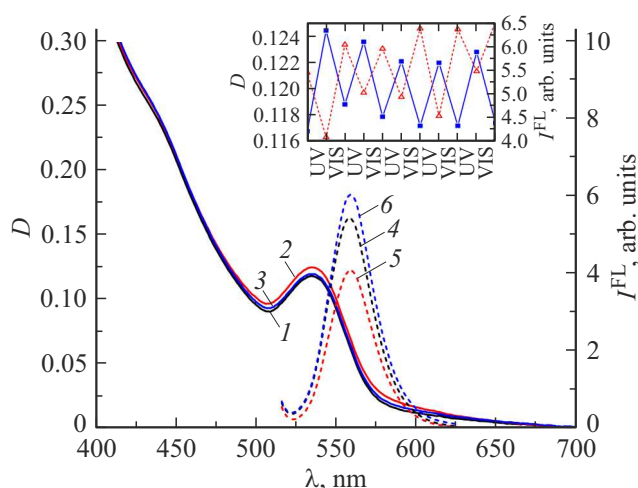


Figure 2. Absorption (curves 1–3) and fluorescence spectra upon excitation at wavelength of 500 nm (4–6) of polymer nanospheres containing QDs and DAE **1** in water before (1, 4), after irradiation with UV (2, 5) and visible (3, 6) light [15]. The insertion shows curves of photoinduced modulation of absorption (blue curves) and fluorescence (red curves) of nanospheres during successive irradiation with UV and visible light.

The results of study of the absorption-fluorescence properties of the synthesized nanospheres in solutions in water are presented in Fig. 2. Changes in the absorption spectra of these samples (the appearance of an absorption band in the 450–650 nm region as a result of UV irradiation) are similar to changes in DAE solutions, which indicates that the photochromic properties of DAE **1** molecules due to reverse photoisomerization of their open and cyclic forms are also preserved in nanospheres.

The radiation parameters of QDs in nanospheres are also modulated due to the isomerization of DAE **1** molecules (Fig. 2). After UV irradiation of solutions of nanospheres, resulting in the formation of cyclic isomers of DAE **1** molecules, their optical density in the visible region of the spectrum increases, while the fluorescence intensity at wavelength of QD radiation decreases, i.e. QD luminescence quenching is observed. As a result of subsequent irradiation with visible light, the reverse process occurs: the optical density decreases, and the fluorescence intensity increases.

Similar photoinduced spectral (absorption and fluorescence) changes are also observed for the synthesized polymer nanospheres based on QDs and DAE **1** embedded in PVA polymer films. The results of a spectral-kinetic study of polymer nanospheres containing QDs and DAE **1** in polymer films are shown in Fig. 3.

As well as the photochromic systems considered above, polymer films containing photochromic nanospheres, when successively irradiated with UV and visible light, exhibit antiphase reversible changes (modulation) in absorption and fluorescence (Fig. 3, insertion). An analysis of the data presented in Figs 1–3 and in the table makes it possible to estimate the efficiency (depth) of fluorescence intensity

modulation by the formula

$$K_{\text{FL}} = 1 - \frac{I^{\text{FL}}}{I_0^{\text{FL}}}. \quad (3)$$

In all systems studied (in different matrices), the observed modulation of QD radiation can be explained both by the effect of an internal filter (reabsorption of QD luminescence by photochrome) and by a change in the quantum yield of QD fluorescence due to the transfer of excitation and (or) charge energy from QDs to molecules of photoinduced cyclic colored form B of DAE **1**, located in the immediate vicinity of QD.

The experimental data obtained make it possible to estimate the attenuation of the QD radiation intensity due to the effect of the internal filter K_{IF} for the three investigated QD-DAE **1** systems:

$$K_{\text{IF}} = 1 - e^{-0.5(\Delta D_{\text{ext}} + \Delta D_{\text{em}})}, \quad (4)$$

where ΔD_{ext} — the change (due to UV irradiation) in the optical density of the sample at the fluorescence excitation wavelength, ΔD_{em} — change (due to UV irradiation) in the optical density of the sample at the fluorescence emission wavelength.

It turned out that the attenuation of radiation due to this effect is 4, 5, and 1% for QD-DAE **1** systems in solution in toluene, in nanospheres in water, and in nanospheres in a PVA polymer film, respectively. In this case, the smallest effect with respect to the overall decrease in the fluorescence intensity (table) is observed for a system containing nanospheres with QDs and DAE **1** embedded in polymer film.

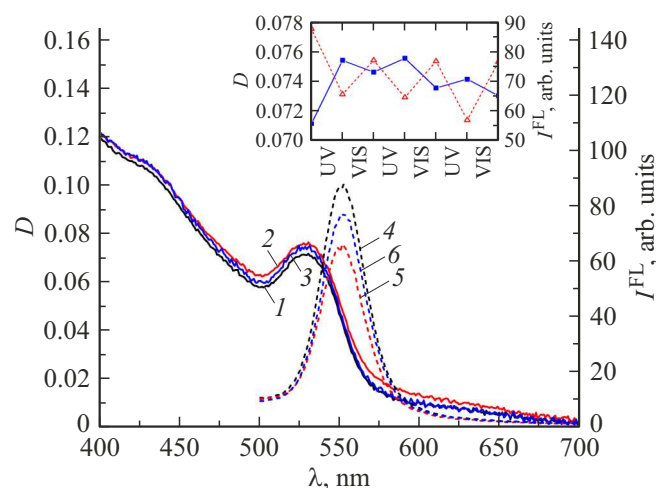


Figure 3. Absorption (curves 1–3) and fluorescence spectra upon excitation of PVA film at a wavelength of 440 nm (4–6) (containing polymer nanospheres with QDs and DAE **1**) before irradiation (1, 4), after irradiation with UV (2, 5) and visible (3, 6) light. The insertion shows curves of photoinduced modulation of absorption (blue curves) and fluorescence (red curves) of nanospheres during successive irradiation with UV and visible light.

Spectral absorption and fluorescence characteristics of photochromic luminescent systems containing CdSe/ZnS QDs and DAE 1

Photochromic luminescent system	λ_A^{\max} , nm	λ_B^{\max} , nm	ΔD_B^{phot}	$\lambda_{\text{QD}}^{\text{FL}}$, nm	I_0^{FL} , a.u.	I^{FL} , a.u.	K_{FL}	K_{IF}	K_{FRET}
Solution in toluene	360	535	0.02	528	169	138	0.18	0.04	0.14
Polymer nanospheres in water	360	555	0.01	553	5.6	4.4	0.21	0.05	0.16
Polymer nanospheres in PVA film	360	558	0.005	552	88	66	0.25	0.01	0.24

Note. λ_A^{\max} , λ_B^{\max} — wavelengths of absorption band maxima of the initial open and photoinduced cyclic form of DAE 1 respectively, $\lambda_{\text{QD}}^{\text{FL}}$ — wavelength of the maximum of the QD fluorescence band; ΔD_B^{phot} — photoinduced change in optical density at the maximum of the absorption band of the photoinduced cyclic form of DAE in the photoequilibrium state; I_0^{FL} , I^{FL} — intensities of the QD fluorescence band before and after UV irradiation, respectively; K_{IF} — contribution to the change in the luminous intensity of the nanospheres of the internal filter effect; K_{FRET} — contribution to the change in the luminous intensity of nanospheres of the FRET effect.

In the absence of other (except for reabsorption and FRET) channels for deactivation of the excited state of QDs, the contribution of the FRET mechanism (K_{FRET}) to the fluorescence intensity modulation can be estimated:

$$K_{\text{FRET}} = K_{\text{FL}} - K_{\text{IF}}. \quad (5)$$

The results of estimating the contributions (shares) of the effect of the internal filter (K_{IF}) and FRET (K_{FRET}) to the change in the luminescence intensity of nanospheres (due to the change in the QD fluorescence quantum yield) are given in the table.

It can be seen from the above results that polymer nanospheres containing QDs and DAE 1 exhibit reversible photoinduced modulation of the fluorescence intensity both in aqueous solution and in films. In this case, photochromic nanospheres exhibit a higher efficiency (depth) of fluorescence intensity modulation and efficiency (contribution) of FRET compared to solution of the QD–DAE 1 system in toluene, even with a significant decrease in the photosensitivity value estimated by the ΔD_B^{phot} parameter (table). The highest parameters were achieved for photochromic nanospheres in a PVA film. Some decrease in the reabsorption contribution for systems in polymer films compared to solutions can be explained by a lower concentration of free DAE 1 molecules not bound to QDs.

Conclusions

For the first time, photochromic polymer films with incorporated polymer nanospheres synthesized by us, containing CdSe/ZnS QDs and DAE 1 molecules, were obtained.

A reversible modulation of the QD fluorescence intensity due to photochromic transformations of DAE 1 molecules and similar to that observed for these photochromic QDs and nanospheres based on them in solutions was found. The contributions of FRET from QD to the colored cyclic DAE 1 isomer and the reabsorption of QD radiation by molecules of the same isomer to the modulation of the QD fluorescence intensity are estimated. It is shown that polymer films with photochromic nanospheres are superior to QD solutions with DAE 1 and nanospheres based on them in terms of the efficiency of fluorescence intensity

modulation and the FRET contribution to it, with a minimal influence of the internal filter effect.

The results obtained are of interest for creation of nanostructured photocontrolled luminescent panels.

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Conflict of interest

The authors declare that they have no conflict of interest.

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