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Polymer nanospheres containing CdSe/ZnS quantum dots and photochromic diaryletenes with photoswitchable luminescence

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A study was carried out and a comparative analysis of the spectral-kinetic (absorption and fluorescent) characteristics of nanospheres containing luminescent inorganic quantum dots (QDs) CdSe/ZnS, covered with an amphiphilic polymer shell, which ensures the stability of nanospheres in aqueous colloidal solutions and the possibility of introducing into them hydrophobic photochromic diarylethene molecules with different structure. Photoinduced reversible isomerization of diarylethene molecules causes modulation of the photoluminescence signal of quantum dots, including through the control of the efficiency of resonant energy transfer (FRET) from quantum dots to the cyclic isomer of diarylethene. The FRET efficiency turned out to be the highest in nanospheres with DAE2 and DAE4. The value of the quality index (QF) of the FRET photomodulator (which shows the efficiency of modulation of the quantum yield of QD photoluminescence), introduced in this work, varies for samples with different diarylethenes from 0.003 (for DAE1) to 0.09 (for DAE2). Nanospheres containing luminescent nanoparticles of various shapes can be used in the development of luminescent photocontrolled panels, fluorescent markers, etc.

Keywords: quantum dots, fluorescence, Förster resonance energy transfer, nanocomposites, photochromism, diarylethenes.

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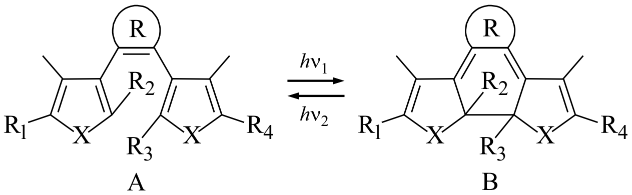
Introduction

As a basis for development of advanced devices in molecular electronics and photonics, photochromic compounds are most suitable, which reversibly change their properties under the action of light and can be used as photoswitches of various types [1]. Thermally irreversible diarylethenes (DAE) [2] are one of the most promising classes of photochromic compounds used for this purpose. Recently, considerable attention has been paid to the study of the properties of photochromic systems and photoinduced fluorescence of organic and inorganic compounds using photochromic substances and Förster resonance energy transfer (FRET) [3–7]. As fluorophores, it is promising to use semiconductor quantum dots (QDs), in particular, CdSe/ZnS of the „core-shell“type [8–19]. They have unique optical properties: a wide spectral region of fluorescence excitation, a narrow fluorescence band, high luminosity and photostability.

The photochromism of DAE consists in the reversible valence isomerization of molecules as a result of the reversible photoinduced transformation of the open form A into the cyclic form B (Scheme 1).



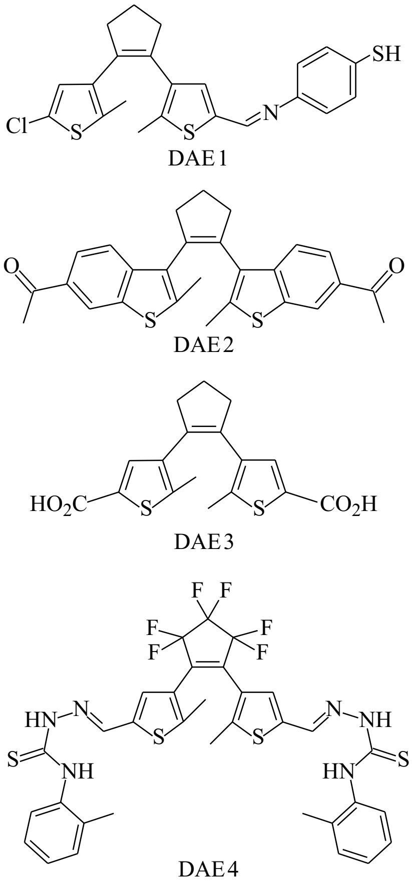
Scheme 1. Photochromic transformations of DAE.

Open colorless isomer A, absorbing UV radiation, is transformed into colored isomer B, which, when exposed to visible radiation absorbed by it, turns into the initial open isomer A. These transformations are carried out only under the action of light absorbed by the corresponding forms of DAE. They are thermally irreversible, since the thermal relaxation of the photoinduced cyclic isomer B into the initial open form A at room temperature does not occur.

In development of previous studies [20–29], this article is devoted to the first comparative spectral-kinetic study of the properties of nanospheres based on CdSe/ZnS QDs with radiation wavelengths of 525, 550, 635 nm and photochromic DAEs of various structures in order to create the scientific basis for development of photochromic radiation nanoswitches.

Experimental part

The objects of study were previously synthesized cyclopentene (DAE1, DAE2, DAE3) and perfluorocyclopentene (DAE4) derivatives of DAE (Scheme 2) [25,29] as well as polymer nanospheres specially synthesized according to a previously developed method [29], including QDs and photochromic DAEs.



Scheme 2.

CdSe/ZnS QDs ($\lambda_{\rm fl} = 525$, 550 and 635 nm) were synthesized at the Research Institute for Physical Chemical Problems of the Belarusian State University, according to an adapted protocol.

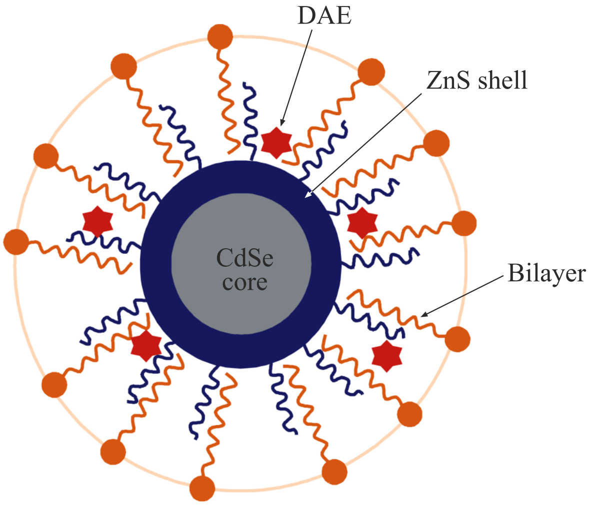


Figure 1. Scheme of the structure of nanospheres with photomodulated fluorescence containing CdSe/(ZnS) QDs and DAE [29].

To obtain polymer nanospheres (Fig. 1) containing complexes of QDs with DAE molecules, we used the method of introducing molecules into a thin polymer shell on the surface of hydrophobic CdSe/ZnS QDs during their encapsulation and solubilization in water using the published procedure [30]. Hydrophobic DAE molecules penetrate into the hydrophobic bilayer on the QD surface, which is formed due to the van der Waals interaction of aliphatic thiol molecules on the QD surface and aliphatic side chains of the poly(maleic anhydride-alt-1-tetradecene) (PMAT) copolymer in chloroform. Further solubilization in water and purification give a stable colloidal solution of the complex of QDs with DAE molecules, which exhibits pronounced photoinduced modulation of QD emission.

The optical characteristics of the objects were studied by spectrophotometry and fluorescence (stationary and kinetic) spectroscopy.

To record absorption spectra in the UV and visible regions of the spectrum, a SPECORD 200 spectrophotometer (Carl Zeiss, Germany) was used, which provides measurement of absorption spectra in the range of 200−900 nm with a discretization step of 1 nm. Possible scattering and reflection from the sample were not taken into account when recording the absorption spectra.

For irradiation of the studied samples, LEDs with emission band maxima at 365 (LED365), 514 (LED514) and 627 nm (LED627) were used. For LED365, LED514, and LED627, the half-widths of the emission bands were 9, 32, and 16 nm, and the optical power was 0.45, 3, and 3 W, respectively. 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 a SM2203 spectrofluorimeter (Solar, Belarus).

Measurements of the fluorescence decay time were carried out on a laboratory setup described earlier [31] operating in the time-correlated photon counting (TCSPC) mode [32]. The excitation source was a PDL 800B picosecond diode laser with LDH-405 and LDH-470 laser heads (PicoQuant, Germany). The registration system included RMA-182 photodetector unit, as well as a system for time-correlated photon counting TimeHarp200 by PicoQuant (Germany). Fluorescence decay curves were recorded with a discretization step of 36 ps. The time resolution of the fluorimeter was ∼ 60 ps.

Results and discussion

Figure 2 shows the optical absorption spectra of solutions of the studied DAEs in the initial and photoisomerized cyclic forms and the fluorescence spectra of QDs. It can be seen in this figure that the cyclic forms of DAE molecules formed after UV irradiation are characterized by absorption bands in the visible region of the spectrum and overlap well with the emission spectra of the selected QDs and, therefore, can be photoexcitation energy acceptors in accordance with the FRET mechanism. According to Förster's theory, the rate constant k_{FRET} of FRET from donor D to acceptor A for a single pair D−A depends on the distance r between D and A:

$$k_{\mathrm{FRET}} = \frac{1}{\tau_{\mathrm{D}}}\left(\frac{R_0}{r}\right)^6, \tag{1}$$

where τ_{D} — the lifetime of the excited state of the donor in the absence of an acceptor; R_0 — characteristic distance, called Förster radius, at which the transfer efficiency is 50%.

The Förster radius R_0 (in Å) was evaluated according to the expression

$$R_0 = 0.211(\kappa^2 n^{-4} Q_{\mathrm{D}} J(\lambda))^{1/6}, \tag{2}$$

where κ_2 — a factor describing the mutual spatial orientation of the dipole moments of the D and A transitions, n — the refractive index of the medium, Q_{D} — quantum yield D in the absence of an acceptor, $J(\lambda)$ — overlap integral reflecting the degree of spectral overlap between emission D and absorption A,

$$J(\lambda) = \int\limits_0^\infty F_{\mathrm{D}}(\lambda)\varepsilon_{\mathrm{A}}(\lambda)\lambda^4 d\lambda, \tag{3}$$

$F_{\mathrm{D}}(\lambda)$ — normalized fluorescence intensity D, $\varepsilon_{\mathrm{A}}(\lambda)$ — extinction coefficient A.

Let us consider the results of studying the photochromic properties of the synthesized nanospheres in solutions presented in Fig. 3 and in the table. After UV irradiation of these solutions, changes in the absorption spectra are observed, similar to those that occur in DAE solutions (Fig. 2): absorption bands appear in the visible region of the spectrum, overlapping with the emission spectra of QDs contained in nanostructures. Thus, changes in the absorption spectra of DAE in the composition of the synthesized nanospheres upon irradiation of particles with UV and visible light are qualitatively similar to those for DAE solutions, and therefore it can be concluded that, under these conditions, DAE molecules exhibit photochromic properties due to the reverse photoisomerization of their open and cyclic forms.

Comparing the absorption spectra of cyclic forms of DAE formed in the composition of nanospheres and in solutions, it should be noted that the absorption bands of DAE in nanospheres are shifted in comparison with their spectra in chloroform for some samples to the long wavelength side, and for others — to the short wavelength. Thus, the absorption bands of DAE1 and DAE4, which have SH- or S-groups as side substituents, experience a bathochromic shift, which may indicate the chemical interaction of these DAE molecules with QDs. At the same time, the absorption bands of DAE3 are shifted to the short wavelength region, which can be explained by the weaker interaction of molecules with the environment in nanospheres compared to chloroform. The absorption spectra of DAE2 in nanospheres and in chloroform are almost identical.

The fluorescence parameters of QDs in nanospheres are sensitive to the isomerization of DAE molecules. This is demonstrated by the data on the effect of successive UV and visible light irradiation on the optical density and fluorescence intensity of nanosphere solutions presented in Fig. 3, *a−d* and in the table.

As can be seen in Fig. 3, *a−d*, after UV irradiation of nanosphere solutions, their optical density in the visible region of the spectrum increases, which indicates formation of cyclic isomers of DAE molecules, and the fluorescence intensity at the QD radiation wavelength decreases in this case, i.e. QD luminescence quenching is observed. After subsequent irradiation with visible light, the reverse process occurs: the optical density decreases, and the fluorescence intensity increases. Such antiphase changes in the optical density and fluorescence intensity are repeated after subsequent cycles of photoirradiation of the samples with UV and visible light (Fig. 3, *e−h*). Obviously, the reversible photoisomerization of DAE1 molecules during irradiation with UV and visible light, which results in formation and disappearance of an absorption band in the visible region of the spectrum, leads to modulation of the fluorescence intensity of QDs localized in nanospheres.

Modulation of fluorescence intensity may be due to changes in the quantum yield of QD fluorescence due to the transfer of excitation and/or charge energy to DAE molecules located in close proximity, as well as an internal filter effect (i.e., absorption of fluorescence light quanta by DAE molecules in cyclic form).

To obtain information on the contribution of FRET to the modulation of the fluorescence intensity of QDs by DAE molecules in nanospheres, we studied the kinetics of the decay of QD fluorescence before and after irradiation with UV and visible light. Changes in the

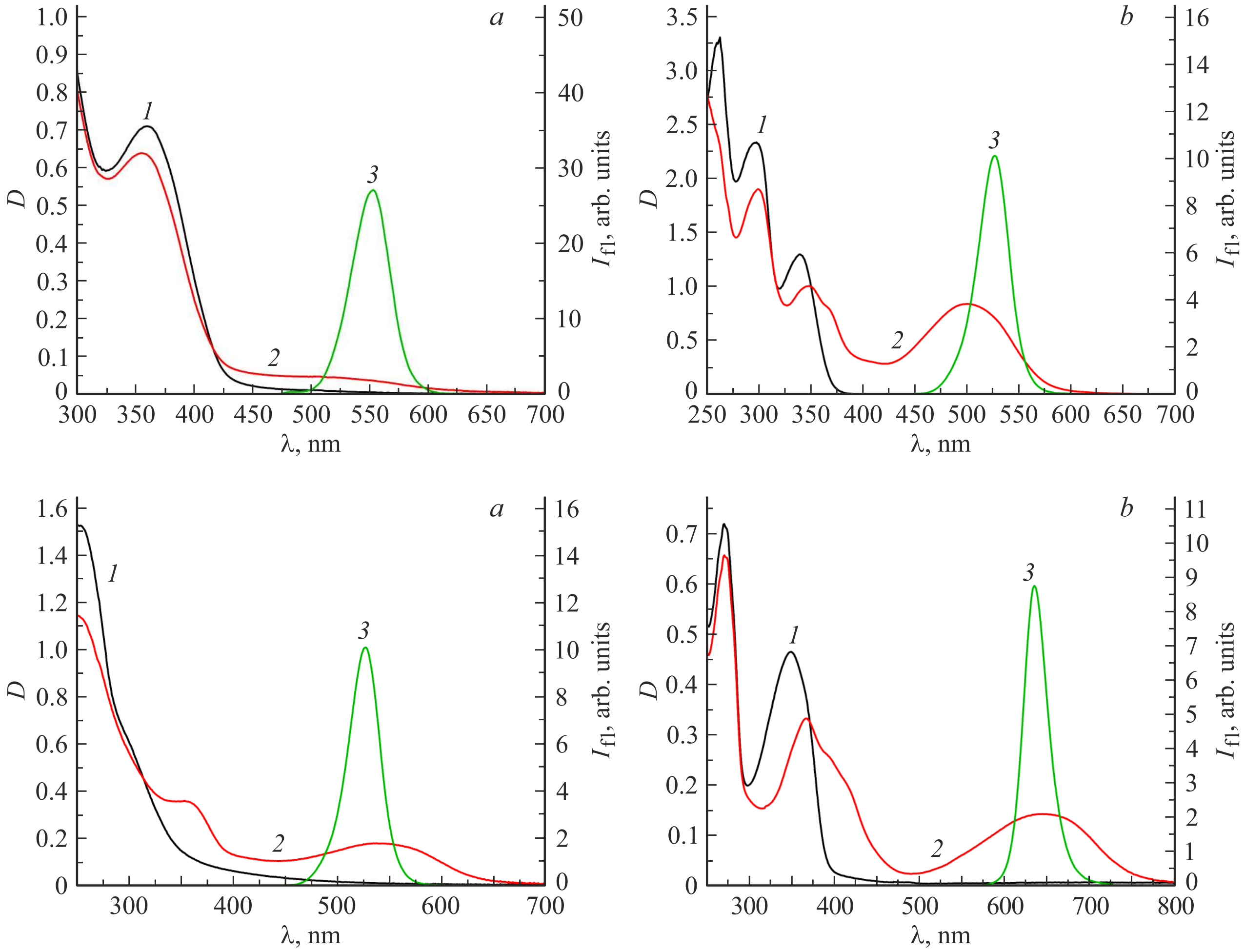


Figure 2. Absorption spectra of DAE1 (*a*) [29], DAE2 (*b*), DAE3 (*c*), DAE4 (*d*), in toluene (*a*) and chloroform (*b, c, d*) in the initial (*1*) and photoisomerized cyclic form (*2*), as well as fluorescence spectra (*3*) of CdSe/ZnS QDs.

Spectral-kinetic and other characteristics of photoactive components of synthesized nanospheres

Photoactive components of nanospheres	λ^{fl}_{QD}, nm	λ^{max}_{A}, nm	λ^{max}_{B}, nm	ΔD^{phot}_{B}	$\langle\tau^{\alpha}_{0}\rangle$, ns	$\langle\tau^{\alpha}_{UV}\rangle$, ns	$\langle\tau^{\alpha}_{VIS}\rangle$, ns	$E(F)$	$E(\tau^{\alpha})$	Q_0	QF
KT550-DAE1 [29]	553	360 (360)	555 (525)	0.01	4.6	4.4	5.0	0.22	0.16	0.02	0.003
KT525-DAE2	528	341 (339)	500 (500)	0.07	12.2	6.5	11.7	0.49	0.41	0.21	0.09
KT525-DAE3	527	243 (254)	505 (543)	0.004	7.4	5.8	7.4	0.23	0.22	0.11	0.02
KT635-DAE4	636	361 (350)	675 (645)	0.05	0.8	0.4	1.1	0.63	0.67	0.02	0.01

Note. λ^{max}_{A}, λ^{max}_{B} — wavelengths of the maxima of the absorption bands of the initial open and photoinduced cyclic forms of DAE (in brackets — in chloroform solution), λ^{fl}_{QD} — wavelength of the QD fluorescence band maximum; ΔD^{phot}_{B} — photoinduced change in optical density at the maximum of the absorption band of the photoinduced cyclic form of DAE in the photoequilibrium state (photosensitivity); $\langle\tau^{\alpha}_{0}\rangle$, $\langle\tau^{\alpha}_{UV}\rangle$, $\langle\tau^{\alpha}_{VIS}\rangle$ — average QD lifetime (by amplitude) before irradiation, after UV irradiation, and after irradiation with visible light, respectively; Q_0 — quantum yield of QDs in nanospheres with DAE before irradiation; QF — FRET photomodulator quality index.

average fluorescence lifetime of QDs in nanospheres upon photoisomerization of DAE molecules contained in them may be an indicator of the manifestation of the FRET mechanism.

As an example, Fig. 4, *a* shows the fluorescence decay curves of aqueous solutions of nanospheres containing QDs and DAE2 before and after UV and visible irradiation. Changes in the fluorescence lifetime are also repeated after

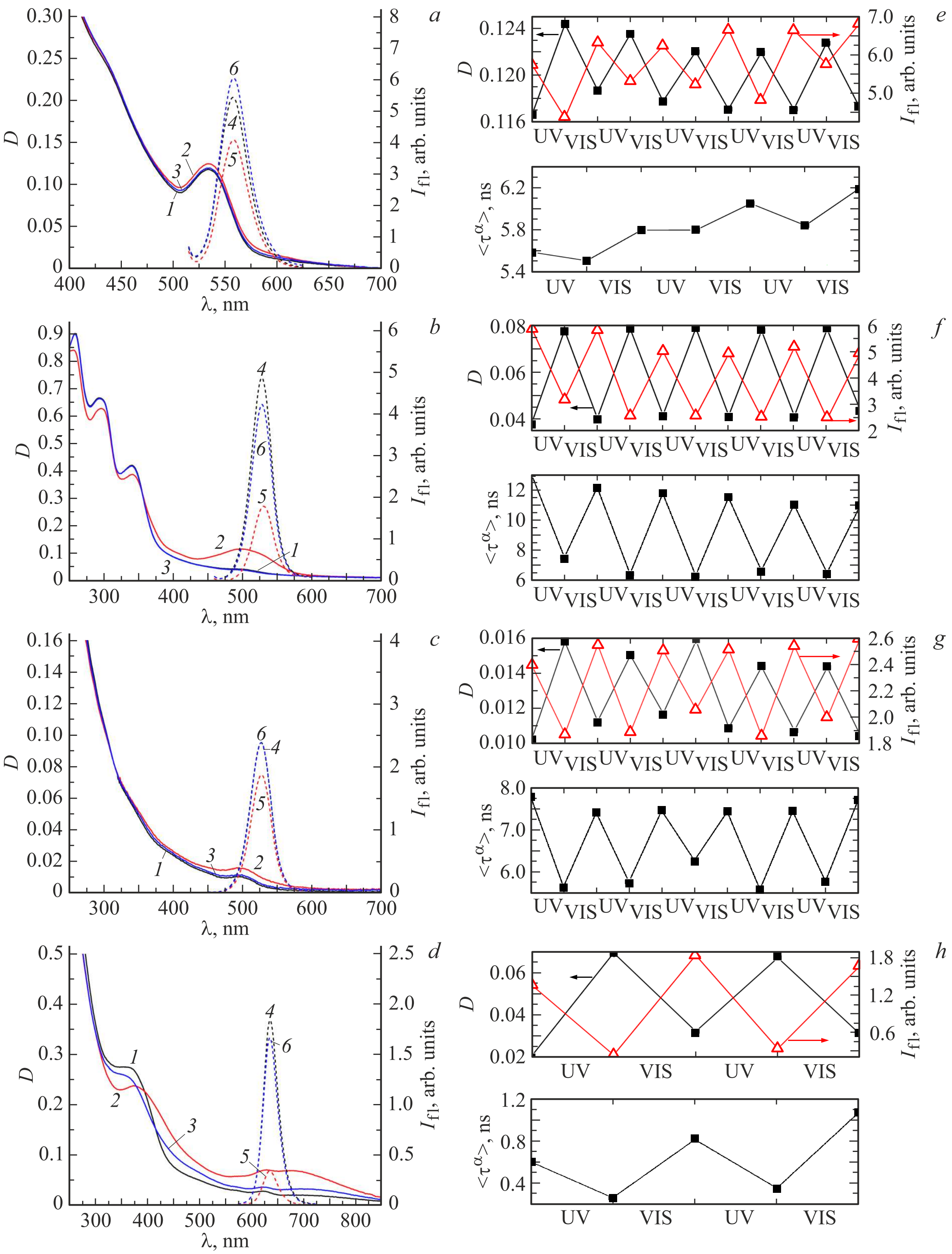


Figure 3. *a–d* — absorption (*1–3*) and fluorescence (*4–6*) spectra of polymer nanospheres containing QD550 and DAE1 (*a*) [29], QD525 and DAE2 (*b*), QD525 and DAE3 (*c*), QD635 and DAE4 (*d*), in water before (*1, 4*), after irradiation with UV (*2, 5*) and visible (*3, 6*) light. *e–h* — changes in the optical density D at the absorption maximum of the cyclic form of DAE, the intensity I of fluorescence at the maximum of the QD emission band, and the average lifetime $\langle\tau^{\alpha}\rangle$ of QD fluorescence for polymer nanospheres containing QD550 and DAE1 (*e*) [29], QD525 and DAE2 (*f*), QD525 and DAE3 (*g*), QD635 and DAE4 (*h*), after successive irradiation with UV ($\lambda = 365$ nm) and visible ($\lambda = 514$ nm (*e,f,g*), $\lambda = 627$ nm (*h*)) light.

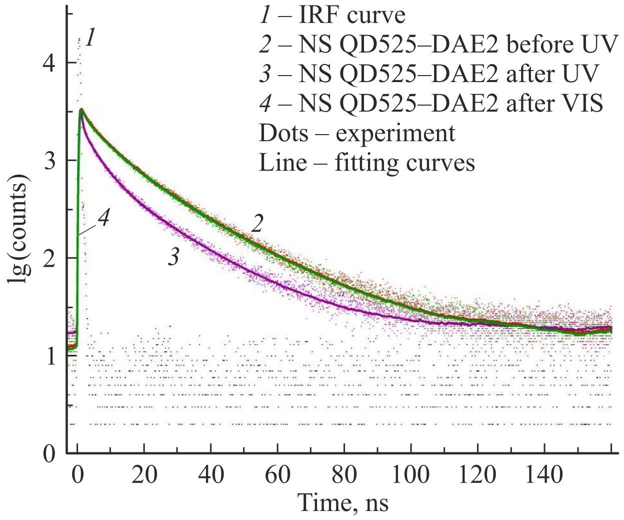


Figure 4. Fluorescence decay curves of aqueous solutions of nanospheres containing QD525 and DAE2 before (*2*) and after UV (*3*) and visible (*4*) irradiation.

subsequent cycles of photoirradiation of the samples with UV and visible light (Fig. 3, $e{-}h$). For all QD samples, the fluorescence decay curves can be satisfactorily described using at least three exponential components. We do not associate these kinetic components with any specific elementary emitters (or groups of emitters), and as an estimate of the lifetime of the QD excited state, we will use expressions for the average lifetimes $\langle\tau\rangle$.

The FRET efficiency for D surrounded by n molecules A (DAE) can be calculated based on measurements of the fluorescence lifetime using the formula

$$E(\tau) = 1 - \frac{\tau_{\mathrm{DA}n}}{\tau_{\mathrm{D}}}. \qquad (4)$$

This expression is valid for monoexponential decay. However, in our case, the fluorescence kinetics is multi-exponential, so we can use the average lifetime (by the $\langle\tau\rangle$ contribution or by the amplitude $\langle\tau^{\alpha}\rangle$) to characterize the fluorescence decay time.

The quenching of QD fluorescence by cyclic DAE isomers in nanospheres caused by FRET and a combination of other factors (in particular, reabsorption) can be characterized by the integrated quenching efficiency parameter $E(F)$, which can be calculated based on measurements of the fluorescence intensity:

$$E(F) = 1 - \frac{F_{\mathrm{DA}}}{F_{\mathrm{D}}}, \qquad (5)$$

where F_{D} — fluorescence intensity D (QD), F_{DA} — fluorescence intensity of D in the presence of A (cyclic DAE isomer).

When comparing the results of the estimate $E(\tau)$ for $\langle\tau\rangle$ and $\langle\tau^{\alpha}\rangle$ and comparing it with the experimental data, it turned out that the estimate $E(\tau^{\alpha})$ correlates better with the results of fluorescence intensity modulation $E(F)$. Therefore, further, the $\langle\tau^{\alpha}\rangle$ parameter (average lifetime of QD fluorescence by amplitude) was used to estimate the average lifetime and calculate the FRET efficiency,

$$\langle\tau^{\alpha}\rangle = \frac{\sum_i \alpha_i\tau_i}{\sum_i \alpha_i}, \qquad (6)$$

where α_i, τ_i — pre-exponential multiplier and lifetime of i-th component, respectively. The efficiencies of QD quenching $E(F)$ and $E(\tau^{\alpha})$ calculated on the basis of changes in the intensity and lifetime of fluorescence using relations (4) and (5) during DAE photoisomerization in the composition of the studied nanospheres are presented in the table. In the calculations, the averaged values of F and $\langle\tau^{\alpha}\rangle$ from the curves of the cyclic change of these quantities were used (Fig. 3, $e{-}h$). These data show significant reversible changes in the average fluorescence lifetime of QDs due to reversible photochromic transformations of DAE molecules, which indicates a significant contribution of the FRET mechanism to the modulation of QD fluorescence. The greatest changes in the average lifetime are observed for nanospheres containing DAE2 and DAE4. Comparing the efficiency of FRET for nanostructures containing QDs emitting in the green region of the spectrum and as modulating photochromic compounds DAE2 and DAE3, we can conclude that both in terms of the depth of fluorescence intensity modulation and in terms of the contribution to this process, FRET is preferable to DAE2. With the technology used for obtaining nanospheres, it is possible to obtain nanostructures based on luminescent CdSe/ZnS QDs and DAE2 emitting in the green region of the spectrum with a fluorescence intensity modulation depth of about 50%.

For a comprehensive assessment of the effectiveness of nanospheres as fluorescence switches, we introduced the generalizing parameter QF — the quality index of the FRET photomodulator,

$$QF = Q_0 E(\tau^{\alpha}). \qquad (7)$$

The values of this indicator for all studied nanospheres, given in the table, vary from 0.003 (for DAE1) to 0.09 (for DAE2). The difference in the values QF is explained both by the difference in the chemical and optical properties of the DAEs used, and by the difference in the properties of the QDs used. Thus, the presence of active groups in a molecule (DAE1, DAE4) significantly reduces the quantum yield Q_0 of QDs in nanospheres. At the same time, the efficiency of FRET $E(\tau^{\alpha})$ is related to the efficiency of photochromic transformations of the DAE molecule and the extinction coefficient of its colored form B, which enters into the expression for the overlap integral of the absorption spectrum of the DAE colored form B and the QD radiation spectrum. The efficiency of photochromic transformations of DAE can be estimated (based on the parameters given in the table) by the photosensitivity value $\Delta D_{\mathrm{B}}^{\mathrm{phot}}$, the highest value of which (of our samples) is exhibited by diarylethene DAE2. The abovementioned explains why, despite the very good photochromic properties (high light sensitivity $\Delta D_{\mathrm{B}}^{\mathrm{phot}}$) of DAE4 and the highest efficiency of FRET in nanospheres with this compound, the quality index QF turned out to be extremely low (table). And the most effective fluorescence switches due to the FRET effect (among those considered in this article) are nanospheres containing QD525 and DAE2 and having $QF = 0.09$.

Note that there are other reasons related to the photoisomerization of DAE molecules that affect the depth of modulation of the QD fluorescence intensity, which can be associated with the technology used for obtaining nanospheres, the properties of QDs used, and the structure of photochromic molecules. The analysis of these causes is of great practical importance. We are planning such studies in the future.

Conclusions

In this article, we synthesized polymer nanospheres containing CdSe/ZnS QDs and molecules of photochromic DAEs (DAE1, DAE2, DAE3, DAE4), which modulate both the intensity and lifetime of QD fluorescence due to energy transfer during reversible photoisomerization of photochromic molecules. QDs and DAEs in nanospheres are covered with an amphiphilic polymer shell, which ensures good stability of nanospheres in aqueous solutions and the possibility of incorporating hydrophobic DAE molecules.

The dipole-dipole interactions between QDs and DAE molecules associated with FRET make a significant contribution to the modulation of the fluorescence of nanospheres, which is especially pronounced in systems with DAE2 and DAE4.

The concept of the quality index QF of a FRET photomodulator (indicating the efficiency of modulation of the QD fluorescence quantum yield) is introduced. QF is determined both by the QD quantum yield Q_0 in nanospheres with DAE before irradiation and by the FRET efficiency $E(\tau^{\alpha})$. The value of QF varies for samples with different DAEs from 0.003 (for DAE1) to 0.09 (for DAE2). This difference is explained both by the difference in the properties of the QDs used and the difference in the chemical and optical (photochromic) properties of the DAEs used, which in turn affect the values of the quantum yield Q_0 and the FRET efficiency $E(\tau^{\alpha})$.

Nanospheres of this kind, including luminescent nanoparticles of various shapes, can be used in the development of photocontrolled luminescent panels, fluorescent markers, etc.

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Conflict of interest

The authors declare that they have no conflict of interest.

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