Microwave Synthesis of Hybrid Organo-Inorganic Nanosystems Based on CdS Quantum Dots and Photoactive Styrylquinoline Ligand

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Abstract—Hybrid nanosystems (conjugates)—CdS quantum dots with an average diameter of 2.4 nm containing two types of ligands in the organic shell: coordinating (covering) benzyl mercaptan ligand and photoisomerizable styrylquinoline (SQ) ligand, viz., 2-(4-[9-mercaptononoxy]styryl)quinolone—were synthesized in one step by microwave irradiation. The average number of SQ molecules in the hybrid nanosystem shell was found to depend nonlinearly on the relative concentration of this ligand in the starting reaction mixture, the disproportion and cooperative effects being observed upon synthesis. It was shown that, owing to the photoactivity of SQ ligand, the resulting hybrid nanosystems can act as photon switches.

INTRODUCTION

A quantum dot (QD) is a semiconducting nanocrystal whose distinguishing feature is the dependence of absorption and luminescence spectra on the nanocrystal size [1–3]. In order to stabilize and prevent coagulation of quantum dots, their surfaces are covered by a layer of organic ligand. Therefore, even a pure QD is, in fact, a hybrid nanosystem, since it contains organic and inorganic components. But the term "hybrid" nanosystem (conjugate) is generally applied to nanoparticles containing functional organic ligands susceptible to external exposure in the covering shell. Having an effect on such ligands, one can control the properties of hybrid nanosystem as a whole [4]. Of specific interest are hybrid nanosystems with photosensitive ligands whose properties can be controlled easily on exposure to light by changing the light wavelength and intensity and irradiation time [5–7].

To attach a ligand to the QD surface, the ligand must contain special "anchor" groups; for CdS QDs, these can be carboxyl, phosphine, and mercaptan (thiol) groups [8]. Since the functional ligand can decompose under the high-temperature conditions of QD synthesis, hybrid nanosystems are usually synthesized by ligand exchange, for which purpose a colloidal solution of nanoparticles stabilized with an inert (supporting) ligand is mixed with a solution of the functional ligand. As a result of exchange reaction, a portion of the inert ligand molecules are replaced with the functional ones [7].

With the advent of low-temperature synthesis of QDs, including microwave, it became possible to introduce a functional ligand at the step of synthesis of a hybrid nanosystem. In the present work, hybrid organo-inorganic nanosystems QDL_n containing also the photoactive styrylquinoline (SQ) ligand LH (in the form of mercaptide residue L) in the organic shell ("coat") besides the inert (background) BzM ligand were obtained by modification of the earlier developed [9–11] microwave synthesis of CdS quantum dots in the presence of a coordinating (coating) ligand, viz., benzyl mercaptan (BzM). (*E*)-2-(4-[9-Mercaptononoxy]styryl)quinoline (see structure in Scheme 2) containing the thiol "anchor" group as BzM was used as the LH ligand. The concentrations of BzM and cadmium and sulfur precursors in the reaction mixture remained constant and were selected in such a way to produce QDs with a size of 2.4 nm and absorption maximum at 333 nm; the concentration of the photoactive LH ligand varied.

As a result, hybrid QDL_n nanosystems with $n = 0.6–7.7$ were obtained, where n is the average content (number of molecules) of the photoactive ligand in the QD organic shell (determined from absorption spectra).

The parameter n was found to depend nonlinearly on the relative concentration of the photoactive ligand in the starting reaction mixture; the disproportion effect was observed. In addition, the content of the photoactive ligand in the QD shell increased exponentially with an increase in its content in the reaction mixture, and a peculiar cooperative effect was
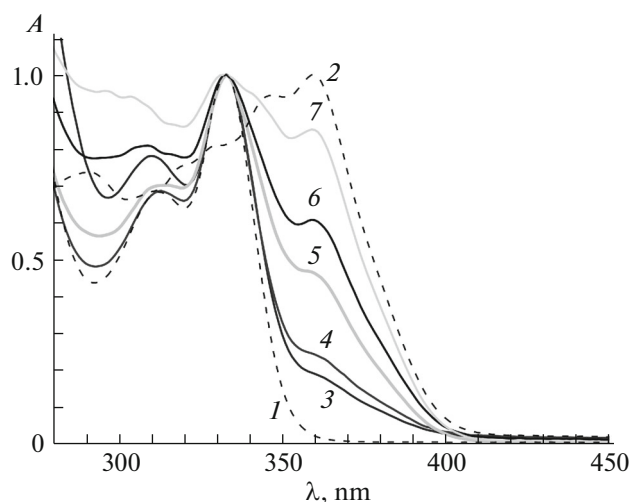
Fig. 1. Absorption spectra in DMF: (*1*) CdS quantum dots with a diameter of 2.4 nm; (*2*) (*E*)-2-(4-[9-mercaptonon-oxy]styryl)quinoline, LH ligand; and hybrid nanosystems: (*3*) sample 1, (*4*) sample 2, (*5*) sample 3, (*6*) sample 4, and (*7*) sample 5; the spectra were normalized to the maximum at 333 nm.

observed. It was shown that, owing to the trans-cis photoisomerization of the SQ group of photoactive ligand, the hybrid QDL_n nanosystems could function as photon molecular switches.

EXPERIMENTAL

The electronic absorption spectra were recorded on a Specord M-400 spectrophotometer and the emission spectra were recorded on a PerkinElmer LS-55 spectrofluorimeter. Spectral and photochemical studies were performed in air-saturated solutions in dimethylformamide (DMF) at room temperature in quartz cells with an optical path length $l = 1$ cm. The fluorescence quantum yields were measured using a diluted alcoholic solution of anthracene whose fluorescence quantum yield was 0.3 [12], the measurement accuracy being 15%. The UV source upon photolysis of solutions was a DRSh-500 lamp whose spectral lines at 313 and 365 nm were isolated using a set of glass filters.

Cadmium acetate dihydrate (Sigma-Aldrich, >98%), thiourea (reagent grade), benzyl mercaptan (Sigma-Aldrich, 99%), DMF (reagent grade), and organic photoactive LH ligand, viz., 2-(4-[9-mercap-tononoxy]styryl)quinoline synthesized as described in [7], were used in the synthesis.

Hybrid QDL_n nanosystems were prepared similarly to the earlier described procedure [11] with addition of the photoactive LH ligand to the reaction mixture. Cadmium acetate dihydrate (13.3 mg, 0.05 mmol) and LH ligand (0.6–3.6 mg, 0.0015–0.009 mmol) were dissolved in DMF (3 mL) and BzM (6 µL, 0.05 mmol)

and then a solution of thiourea (3.8 mg, 0.05 mmol) in DMF (2 mL) were added. The table gives the concentrations of the LH ligand in the reaction mixture in samples 1−5; the concentrations of the remaining precursors in all samples were 10 mM each. The resulted mixture underwent microwave irradiation in an experimental reactor for 40 s.

An aliquot of the solution (1 mL) was sampled to a test tube and ethanol (4 mL) was added. The resulted mixture was centrifuged for 1 h in an OPn-3.02 Dastan centrifuge at the rotation rate of 3000 rpm and the mother liquor was decanted. Ethanol (5 mL) was added to the precipitate remaining at the bottom of the tube, centrifugation was repeated, the mother liquid was decanted, and the resulted precipitate was dried in vacuo. In such a procedure, ligands that were not included in the composition of nanosystem pass to the alcoholic solution owing to a good solubility and the hybrid nanosystem of quantum dots with ligands attached to their surfaces remains in the precipitate, since the CdS nanocrystals are insoluble in ethanol. The resulting samples (white and light yellow powders) of QDL_n hybrids were dissolved in DMF and their spectral-luminescent and photochemical properties were studied.

RESULTS AND DISCUSSION

Figure 1 shows the (normalized) absorption spectra for the "free" CdS quantum dots (whose shell consists of background BzM only, spectrum *1*); free LH ligand, viz., (*E*)-2-(4-[9-mercaptononoxy]styryl)quinoline (spectrum *2*); and resulting hybrid nanosystems, samples 1−5 in the table (spectra *3*−*7*, respectively). The spectrum of quantum dots has a long-wavelength absorption (LWA) maximum at 333 nm, which corresponds to the diameter of 2.4 nm [11], the molar extinction coefficient (MEC) at the maximum being equal to 8×10^4 M^{-1} cm^{-1} (calculated from the empirical dependence of MEC on the QD diameter [13]). The LH ligand has a LWA maximum at 359 nm, the MEC being equal to 2.65×10^4 M^{-1} cm^{-1}. It is obvious that the increase in the absorption at 359 nm (A_{359}, maximum of LH) relative to that at 333 nm (A_{333}, maximum of QD) in the spectra of the hybrid nanosystems in the order "sample 1−sample 5" suggests an increase in the content of the photoactive ligand in QDL_n with an increase in the concentration of this ligand in the starting reaction mixture.

The data from optical spectroscopy were used to calculate the parameter *n*. On the hypothesis that the spectra of QD and LH remain unchanged upon binding of these components to one hybrid nanosystem, the absorbance of QDL_n is defined as

$$A = (\varepsilon_{QD} + n\varepsilon_{L})cl,$$

where ε_i is the MEC of component *i*, *c* is the concentration of HS, and *l* is the optical path length. This
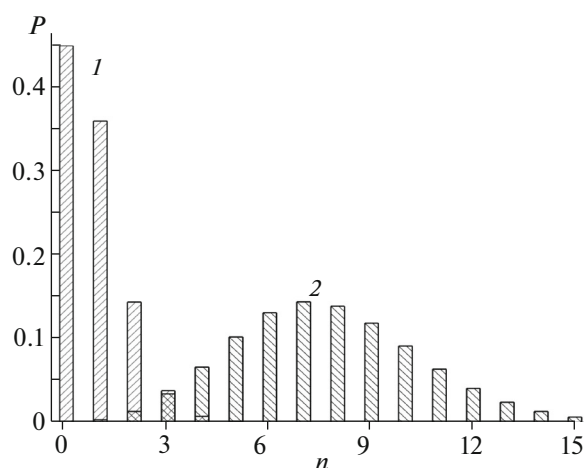
Fig. 2. Distribution of the hybrid nanosystems over the content of photoactive ligand n: the Poisson distribution density function for samples 2 (1) and 5 (2).
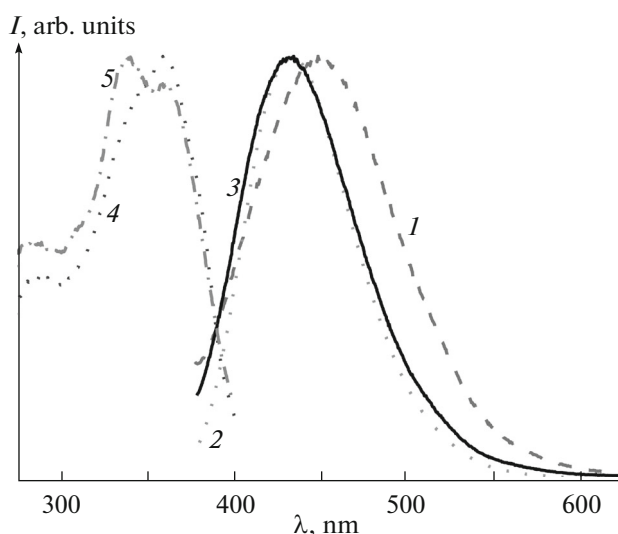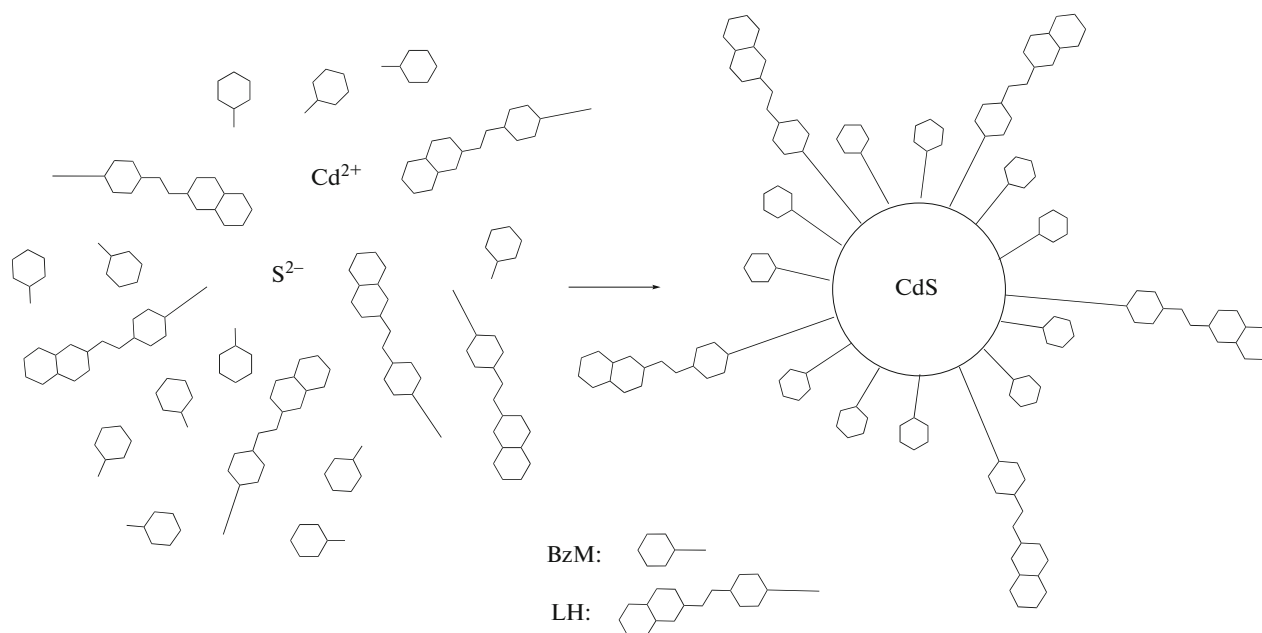

Fig. 3. Luminescence spectra in DMF: (1) CdS quantum dot with a diameter of 2.4 nm (excitation at 330 nm); (2) (E)-2-(4-[9-mercaptononoxy]styryl)quinoline), LH ligand (excitation at 360 nm); (3) hybrid nanosystem, sample 1 (excitation at 330 nm); luminescence excitation spectra of nanosystem 1: (4) observation at 430 nm and (5) observation at 480 nm; the spectra were normalized to the maximum.

equation contains two unknown parameters: n and c. The parameter c can be excluded having taken the ratio of absorbances at two wavelengths λ_1 and λ_2

$$A_1/A_2 = (\varepsilon_{QD,1} + n\varepsilon_{L,1})/(\varepsilon_{QD,2} + n\varepsilon_{L,2}).$$

Hence, we obtain the following equation for calculation of the parameter n:

$$n = (\varepsilon_{QD,1} - (A_1/A_2)\varepsilon_{QD,2})/((A_1/A_2)\varepsilon_{L,2} - \varepsilon_{L,1}). \quad (1)$$

Experimental A_{359}/A_{333} values at the wavelengths of absorption maxima of LH (359 nm) and QD (333 nm) for different samples, as well as the n values calculated by formula (1) are given in the table.

It should be emphasized that the determined n value is the *average* number of photoactive ligand molecules in the hybrid nanosystem. Indeed, there are seven nanosystems of different composition in solution. On the assumption that Poisson's law is applicable in this case, Fig. 2 shows, as an example, the distribution for samples 2 (plot 1) and 5 (plot 2) differing by an order of magnitude in the content of a photoactive ligand. At $n = 0.8$ (sample 2), 45% of nanosystems

Synthesis parameters and conditions of the hybrid QDL$_n$ systems obtained: the concentration (c_{LH}) and relative content (x) of photoactive ligand in the starting solution, the ratio of absorbances (A_{359}/A_{333}) at 359 and 333 nm, and the average number of photoactive ligand molecules (n) in the hybrid nanosystem calculated by formula (1)

No.	c_{LH}, mM	x	A_{359}/A_{333}	n
1	0.3	0.030	0.193	0.6
2	0.6	0.058	0.245	0.8
3	1.2	0.110	0.466	2.1
4	1.5	0.133	0.607	3.4
5	1.8	0.156	0.852	7.7

contain no photoactive ligand and 36% of nanosystems contain 1 molecule of the ligand; at $n = 7.7$ (sample 5) the solution contains virtually equal amounts (~14% each) of nanosystems containing 7 and 8 molecules of the photoactive ligand, and 13% and 12% of nanosystems contain 6 and 9 molecules of ligand, respectively.

The thiol-coated CdS quantum dots were shown earlier to have broad low-intensity luminescence bands in the visible region with a high Stokes shift, which is assigned to recombination of holes with electrons trapped with surface defects (traps), viz., sulfur vacancies [9, 10, 14].

Accordingly, the emission band of CdS quantum dots covered with BzM only has a maximum at 450 nm, Fig. 3, spectrum 1; the luminescence quantum yield of the QD is 0.4%. The styrylquinoline ligand emits at 430 nm with a quantum yield of 3.5%, Fig. 3, spectrum 2. As an example, Fig. 3 shows the luminescence spectra of sample 1. The emission spectrum of hybrid nanosystem, spectrum 3, displays one band with a maximum at 430 nm characterizing mainly the emission of the ligand; upon observation at this wavelength, the luminescence excitation spectrum, Fig. 3, spectrum 4, has one maximum at 360 nm corresponding to the ligand. The contribution of QD to the emission of the hybrid nanosystem is revealed upon observation at the wavelength of 480 nm: the luminescence excitation spectrum, Fig. 3, spectrum 5, contains the long-wavelength maxima corresponding

Scheme 1. Scheme of synthesis of the hybrid QDL$_n$ nanosystem in the presence of ligands of two types in the reaction mixture, benzyl mercaptan (BzM) and (*E*)-2-(4-[9-mercaptononoxy]styryl)quinoline (LH). The ratio between the sizes of particular components of the system corresponds to their real sizes, see the text.

to both the ligand (360 nm) and QD (338 nm) with the latter being predominant.

One of the properties arousing interest in the study of QDL$_n$-type hybrid nanosystems is energy transfer (ET) by inductive resonance between components of the system. The efficient ET requires overlapping of the emission spectrum of one component being an energy donor with the absorption spectrum of another component being an energy acceptor. The comparison between Figs. 1 and 3 shows that the absorption spectra of both components, viz., QD and photoactive ligand, overlap, and their luminescence spectra overlap, but there is no overlap between the absorption spectrum of one component and the emission spectrum of another. The requirement for ET is not fulfilled; i.e., in this case, if the ligand is subjected to exposure, the properties of the whole system will change owing to the change in the properties of the ligand itself.

Let us consider how the synthesis conditions have an effect on the composition of the organic shell. Scheme 1 conventionally shows the formation process and structure of a hybrid QDL$_n$ nanosystem, the sizes of the nanosystem components being proportional to the real ones, which correlate as follows: the QD diameter is equal to 2.4 nm; the van der Waals sizes of ligands along the long axis are 1 nm for BzM and 3 nm for LH (*trans*-isomer) at the fully transoid conformation of the polymethylene chain [7].

The question is whether the relative content of the photoactive ligand in the hybrid nanosystem corresponds to its relative content in the reaction mixture. The portion (x) of the photoactive ligand in the starting solution (S) is set by the synthesis conditions and defined by the concentration ratio $x = c_{LH}/(c_{BzM} + c_{LH})_S$, where c_i is the concentration of component i. The portion (y) of the photoactive ligand in the hybrid nanosystem (QDL) is defined by the relation $y = n/(N_{BzM} + n)_{QDL}$, where N_{BzM} is the number of benzyl mercaptan molecules in the QD shell. As shown above, another parameter, viz., the average number (n) of photoactive ligand molecules in the QD shell in the hybrid nanosystem, is determined experimentally from the absorption spectra. To determine the dependence of n on x, one should take into account that both ligands, BzM and LH, contain thiol "anchor" groups of the same type, which results in two consequences. First, the ligands compete for the same coordination centers at the QD surface, where the number of such centers is determined by the size of the QD. Assuming that in all hybrid nanosystems under study the coordination sites are occupied completely, we find that the total number of ligands in the HS shell is constant and equal to $N_{BzM, 0}$, and the number of BzM molecules in the pure QD is $(N_{BzM} + n)_{QDL} = N_{BzM,0}$. Second, since the ligands are of the same type, they are incorporated into the shell of the growing QD with equal probabilities to form a mixed monomolecular layer. In such case, one should expect the equality $y = x$, whence we get the directly proportional relationship
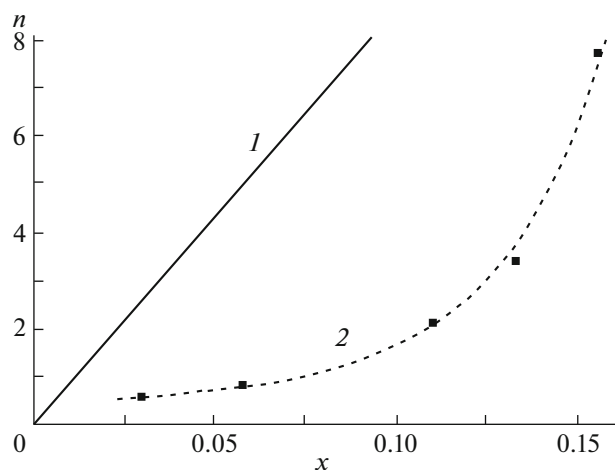
$$n = N_{BzM, 0} x. \tag{2}$$

Fig. 4. Average number of photoactive ligand molecules (n) in the quantum dot shell in the hybrid QDL_n system as a function of the relative content (portion) of this ligand in the starting reaction mixture (x): (*1*) theoretically calculated dependence $n = 86x$ under the condition of equally probable additions of ligands of two types (see the text) and (*2*) experimental dependence found from the ratio of absorption bands; the dashed line shows the approximation of exponential function (see the text).

In [7], on the assumption that BZM forms a close-packed monolayer at the QD surface, the average number of BzM molecules in the shell of the CdS QD with a diameter of 2.4 nm was calculated to be 86 (the cross-sectional area of BzM was taken equal to 0.21 nm^2); i.e., $N_{BzM, 0} = 86$, whence $n = 86x$.

The experimental relationship between the average number of photoactive ligand molecules in the QD shell in the hybrid nanosystem and the relative content (portion) of this ligand in the starting reaction mixture is shown in Fig. 4.

As Fig. 4 shows, the points on the initial section of the experimental curve *2* lie significantly lower than the theoretical line *1*, which was calculated by the equation $n = 86x$. At lower x, the amount of photoactive ligand entering the QD shell is less than that expected from the proportionality condition. The second effect observed is a nonlinear increase in the parameter n with an increase in x. The dashed line in Fig. 4 shows the approximation of the experimental points by the function

$$n = 0.55\exp(107x^2).$$

The correlation coefficient of the approximation is equal to 0.999; however, if even a phenomenological model is absent, the physical sense of the relationship found is unclear.

The fact that the experimental points lie below the theoretical straight line can be explained by overestimation of the $N_{BzM, 0}$ value. The value of 86 was obtained in terms of the "geometrical model" under
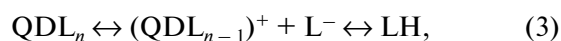
the assumption that BzM completely fills the QD surface to form a close-packed layer. It is clear that this value is overestimated. The thiol ligand coordinates to the cadmium ions, which alternate with the sulfur ones at the nanocrystal surface. The ratio between the cadmium and sulfur ions at the surface depends on a certain face and can change within a wide range. For example, let us consider the extreme case where one crystal face contains only cadmium ions. In such a case, only sulfur ions will be on the opposite face of the nanocrystal, which follows from the mass balance and electroneutrality conditions of QD. Consequently, the cadmium ions cannot occupy the whole surface of QD; i.e., $N_{BzM,0}$ should be less than 86.

With regard to disproportionality between the ratios of functional and background ligands in the solution and nanoparticle shell, this effect was noted earlier upon adsorption of mercaptan ligands at the surface of gold nanoparticles [15]. The authors explained this effect by attraction or repulsion between molecules of two types or by the different degree of their solvation, since the ligands had significant difference in the structure: one ligand contained only the aliphatic radical and the other ligand contained additionally the hydroxyl group.
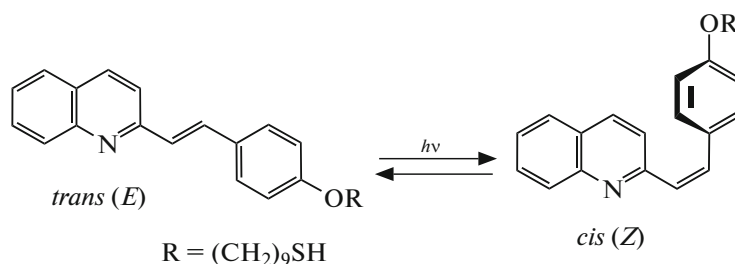
In this case, we use ligands of the same type which have aromatic and aliphatic fragments which are close in chemical nature; therefore, disproportional inclusion of the ligands in the organic shell of QD cannot be explained by the difference in their solvation properties. Possibly, some features of microwave synthesis are manifested in this effect (see below).

The upward deviation of curve *2* in Fig. 4 suggests that the addition of each following molecule of the SQ ligand to QD occurs more easily than that of previous one, i.e., there is a peculiar cooperative effect. During self-association of dyes, nucleic bases, and surfactants, the cooperative effect is characterized by the fact that, after the formation of a dimer, the addition of following molecules to a growing aggregate is facilitated, which is expressed in the increase in the association constant.

To estimate the association constant of the SQ ligand, sample 1 was kept in DMF for one day and then the HS was precipitated with ethanol and spilled off. No spectrally detectable amounts of the SQ ligand were observed in the mother liquid. Taking the detection limit as equal to the error of absorbance measurement (0.001), one can estimate that the stability constant for HS as a complex corresponding to the equilibrium

$$QDL_n \leftrightarrow (QDL_{n-1})^+ + L^- \leftrightarrow LH, \qquad (3)$$

has a value of $K > 10^9$ M^{-1} at room temperature, i.e., the HS is a quite stable formation. The fact that process (3), at least from right to left, is carried out under the conditions of microwave synthesis follows from the absorption and luminescence spectra of HS. It is

Scheme 2. Photoisomerization of styrylquinoline photochrome in the LH ligand.
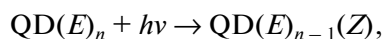
possible that the entry of ligands to the QD shell upon synthesis is not thermodynamically equilibrium, but is kinetically controlled and defined by activation of molecules of the corresponding ligand on exposure to microwave radiation. In this case, the difference in the structure of ligands of two types, BzM and LH, results in different degrees of their activation. Since the activating action of microwave radiation is related to the dipole moment of a molecule, the dipole moments of ligands were calculated by the B3LYP/6-31G* density functional theory (DFT) [7] to be 1.64 D for BzM and 3.99 D for LH (at the fully transoid conformation of the polymethylene chain). Different degrees of ligand activation result in violation of the condition of their equally probable incorporation into the shell of the growing QD, which was used upon derivation of formula (2).

Note that the model of kinetically controlled formation of the HS organic shell can explain the disproportion effect, but does not explain the cooperative one. This effect is obviously due to the interaction of SQ ligands with each other, which manifests itself upon an increase in the ligand concentration.

The styrlquinoline ligand LH was used for the synthesis of hybrid nanosystems, since the SQ photochrome group itself is a photon molecular switch, because it exists as two thermally stable isomers, *trans-* and *cis-*isomer, capable of interconversion on exposure to light. Scheme 2 shows the reversible photoisomerization by the example of a free LH ligand.

The combination of two SQ fragments to the bichromophoric diad gives a system existing in three stable states, owing to which it can simulate the effect of double-address switches, viz., logic gates [16]. By analogy with this, the hybrid QDL_n nanosystem is an n-address photon switch. The extreme states of the nanosystem are $QD(E)_n$ containing only the *trans-* (E)-isomers of the photoactive ligand and $QD(Z)_n$ containing only the *cis-*(Z)-isomers.

On exposure of $QD(E)_n$ to light, photoisomerization occurs

$$QD(E)_n + h\nu \rightarrow QD(E)_{n-1}(Z),$$

isomerization of any one of the ligands being equally probable; i.e., there are n structures with the $QD(E)_{n-1}(Z)$ composition. Which of the ligands underwent isomerization can be determined, for example, by electron microscopy upon the study of a single QD (hybrid nanosystem) attached to any matrix or surface. One cannot determine the structure of the photolysis product by electron microscopy (absorption or emission), since the absorption and luminescence spectra for all n structures of the $QD(E)_{n-1}(Z)$ composition are identical (to be more exact, there can be some differences related, for example, to interaction of ligands with each other at the QD surface at high n).

Upon subsequent irradiation of $QD(E)_{n-1}(Z)$, reversible isomerization to $QD(E)_n$ can occur (the probability of this reaction is determined by the portion of light absorbed with the Z-isomer), but the main process is isomerization of the second E-SQ group and so forth. Thus, in theory, the number of states for the system of n switches each of which can be in two states reaches the value of 2^n. However, we can distinguish only the $(n + 1)$ state of the hybrid QDL_n nanosystem, since spectral measurements in solution can determine only the number of ligands that entered the reaction, but not the definite structure of the nanosystem that formed.

The simulation studies in solution impose an additional restriction, viz., the *trans-*isomer cannot be transformed to the *cis-*isomer and vice versa on exposure to light owing to the photoisomerization reversibility. On exposure to light with a wavelength λ, the spectral changes terminate after reaching the photostationary state (PS_λ) consisting of the mixture of *trans-* and *cis-*isomers whose ratio depends on the MECs of these isomers and quantum yields of trans-cis and cis-trans photoisomerizations.

The SQ ligand (LH) was shown earlier to afford spectrally distinguishable PSs on exposure to light with wavelengths of 313 and 365 nm, since PS_{313} and PS_{365} contain 38% and 14% of the *trans-*isomer (in chloroform), respectively [7]. In DMF, the difference between PSs is slightly less: the content of *trans-*isomer is 32% and 14% for PS_{313} and PS_{365}, respectively, but it is sufficient for simulation of the effects of photon molecular switches. We used the hybrid nanosystem 5 as a model of such a switch.
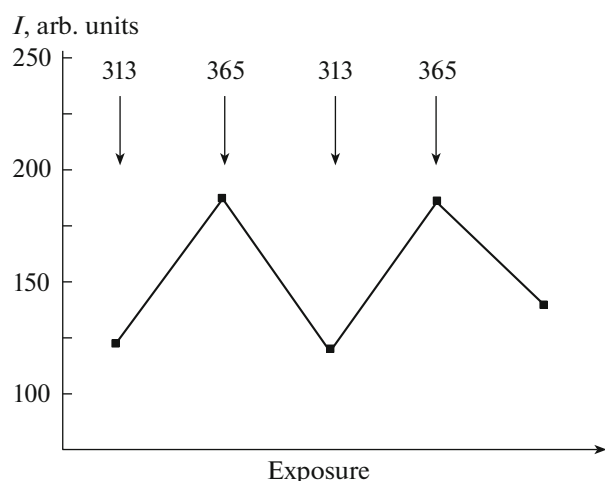
I, arb. units

Fig. 5. Change in the luminescence of nanosystem 5 at 430 nm (excitation at 360 nm) on successive exposure to light with a wavelength of 313 and 365 nm. The initial state is PS_{365}.

The acting input signal transforming from one state to another one is irradiation with light of 313 nm. Irradiation with light of 365 nm resets the switch to the initial state (reset function). The output signal is the luminescence intensity at the wavelength of 430 nm (upon excitation at 360 nm) or absorbance at 360 nm.

At first, we obtained the initial state of switch, viz., PS_{365}, enriched with the *cis*-isomer and, therefore, possessing a dull fluorescence. Upon subsequent irradiation with a light of 313 nm, cis-trans photoisomerization occurred until reaching PS_{365}, the PS where the portion of the *trans*-isomer possessing fluorescence increased, which resulted in a rise in the intensity of the output signal.

Figure 5 shows the change in the luminescence intensity at the wavelength of 430 nm (the emission maximum of LH) upon switching of sample 5 between PS_{313} and PS_{365}. The analogous plot is obtained when the absorbance at 360 nm is used as the output signal.

Calculations show that the change in the absorbance and luminescence on going from PS_{365} to PS_{313} and vice versa is 16−18% of the total range of variation of these parameters upon complete photoisomerization of all SQ ligands (on going from $QD(E)_n$ to $QD(Z)_n$). Since sample 5 contains on average about 7−8 molecules of the SQ ligands in the QD shell, the reversible transition between PS_{365} and PS_{313} formally corresponds to photoisomerization of 1−2 molecules of SQ ligands (16% of 13). To involve a higher number of ligands in the same nanosystem in model experiments, it is necessary to use other photostationary states.

CONCLUSIONS

Thus, we showed that the hybrid organo-inorganic nanosystems (conjugates) based on CdS quantum dots containing two types of ligands, benzyl mercaptan as the background ligand and mercaptononoxystyrylquinoline (SQ) as the photoactive ligand, can be obtained in one step under the conditions of microwave synthesis. The composition of the organic shell, i.e., the relative contents of ligands, is controlled by their concentrations in the starting reaction mixture.

The average number of SQ molecules in the shell of the hybrid nanosystem was found to depend nonlinearly on the relative concentration of this ligand in the starting reaction mixture, the disproportion and cooperative effects being observed in the synthesis. The effects observed are assumed to be related to the microwave activation features of ligands which are incorporated into the quantum dot shell as a result of a kinetically controlled process rather than a thermodynamically controlled one.

Being a part of the organic shell, the SQ ligand retains photoisomerization ability, owing to which the hybrid nanosystems obtained can function as photon molecular switches.

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