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Article

Effect of pH and ionic strength on the photoluminescence of size-fractionated AgInS₂/ZnS quantum dots

T. S. Ponomaryova[✉], V. V. Olomsкая, A. S. Novikova, I. Yu. Goryacheva

Saratov State University, 83 Astrakhanskaya St., Saratov 410012, Russia

Tatiana S. Ponomaryova, tatyanka.ponomareva.97@mail.ru, <https://orcid.org/0000-0002-8472-4596>

Vera V. Olomsкая, o-v-v99@mail.ru, <https://orcid.org/0000-0001-9065-1648>

Anastasiya S. Novikova, novikova.anastasiya.18@mail.ru, <https://orcid.org/0000-0002-8444-5562>

Irina Yu. Goryacheva, goryachevaiy@mail.ru, <https://orcid.org/0000-0003-1781-6180>

Abstract. Background and Objectives: Cellular labeling with fluorescent molecules appears to be one of the key methods of cell biology that continues to evolve with the advent of new fluorescent probes possessing unique properties. Ternary AgInS₂/ZnS quantum dots occupy a special position compared to other fluorescent molecules due to their size-adjustable photoluminescence combined with broadband excitation and long emission lifetime. For the use of quantum dots of AgInS₂/ZnS composition as a fluorescent probe in *in vitro* applications, they should have low physiological toxicity and good stability in physiological pH range. The objective of this work is therefore to evaluate the change of photoluminescent properties of AgInS₂/ZnS quantum dots with changing pH of the medium and ionic strength. **Materials and Methods:** To evaluate the effect of pH and ionic strength on the photoluminescence properties of AgInS₂/ZnS quantum dots, a size-selective precipitation procedure was carried out and the photoluminescence and absorption spectra of the quantum dot fractions were analyzed. **Results:** Ternary photoluminescent AgInS₂/ZnS quantum dots stabilized in water by thioglycolic acid have been obtained by direct synthesis. Size-selective precipitation allowed to discriminate of 11 AgInS₂/ZnS quantum dots fractions from the initial ensemble, revealing distinctly various optical properties. The effect of different pH and ionic strengths on the photoluminescent properties of AgInS₂/ZnS quantum dots fractions has been studied. While in strong acidic and basic media the dramatic changes have been observed, the pH and ionic strength range corresponding to the biological fluids has shown no significant influence on the photoluminescent properties of all quantum dots fractions. **Conclusion:** This indicates the potential application of these nanoobjects as photoluminescent probes in various bioapplications. **Keywords:** photoluminescence, ternary quantum dots, pH, ionic strength, stability

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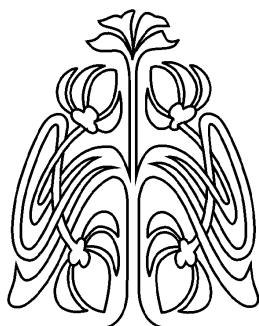
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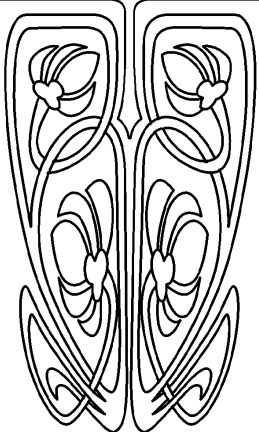
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Влияние pH и ионной силы на фотолюминесценцию
фракционированных по размеру квантовых точек AgInS₂/ZnS

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НАУЧНЫЙ
ОТДЕЛ





Т. С. Пономарева[✉], В. В. Оломская, А. С. Новикова, И. Ю. Горячева

Саратовский национальный исследовательский государственный университет имени Н. Г. Чернышевского, Россия, 410012, г. Саратов, ул. Астраханская, д. 83

Пономарева Татьяна Сергеевна, аспирант кафедры общей и неорганической химии Института химии, tatyanka.ponomareva.97@mail.ru, <https://orcid.org/0000-0002-8472-4596>

Оломская Вера Владимировна, магистрант кафедры общей и неорганической химии Института химии, o-v-v99@mail.ru, <https://orcid.org/0000-0001-9065-1648>

Новикова Анастасия Сергеевна, кандидат химических наук, младший научный сотрудник лаборатории неорганической химии Института химии, novikova.anastasiya.18@mail.ru, <https://orcid.org/0000-0002-8444-5562>

Горячева Ирина Юрьевна, доктор химических наук, профессор кафедры общей и неорганической химии, директор Института химии, goryachevaiy@mail.ru, <https://orcid.org/0000-0003-1781-6180>

Аннотация. Маркировка клеток флуоресцентными молекулами представляется одним из ключевых методов клеточной биологии, который продолжает развиваться с появлением новых флуоресцентных зондов, обладающих уникальными свойствами. Тройные квантовые точки состава AgInS₂/ZnS занимают особое положение по сравнению с другими флуоресцентными молекулами благодаря регулируемой по размеру фотолюминесценции в сочетании с широкополосным возбуждением и большим временем жизни излучения. Для применения квантовых точек состава AgInS₂/ZnS в качестве флуоресцентного зонда в *in vitro* приложениях они должны обладать низкой физиологической токсичностью и хорошей стабильностью в физиологическом диапазоне pH. Поэтому целью работы является оценка изменения фотолюминесцентных свойств квантовых точек AgInS₂/ZnS при изменении pH среды и ионной силы. Тройные фотолюминесцентные квантовые точки AgInS₂/ZnS, стабилизированные в воде тиогликолевой кислотой, были получены прямым синтезом. Размерно-селективное осаждение позволило выделить из исходного ансамбля 11 фракций квантовых точек AgInS₂/ZnS, проявляющих заметно различные оптические свойства. Исследовано влияние pH и ионных сил на фотолюминесцентные свойства фракций квантовых точек AgInS₂/ZnS. Если в сильнокислой и основной средах наблюдались резкие изменения, то в диапазоне pH и ионной силы, соответствующих биологическим жидкостям, существенного влияния на фотолюминесцентные свойства всех фракций квантовых точек не наблюдалось. Это свидетельствует о возможности использования данных нанообъектов в качестве флуоресцентных зондов в различных биоприложениях.

Ключевые слова: фотолюминесценция, квантовые точки, pH, ионная сила, стабильность

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1. Introduction

Semiconductor nanocrystals – quantum dots (QDs) can play an important role in many applications, such as living cells and tissues bioimaging, targeted drug delivery, immunoassays, biosensors [1–3]. Many of these applications have been developed using cadmium and lead chalcogenides based QDs, but their cells and tissues toxicity are a concern [4]. Compared to binary QDs, indium-based ternary QDs, particularly CuInS₂ and AgInS₂ (AIS), combine high photostability, high optical absorption, large Stokes shift, wide absorption and photoluminescence (PL) bands [5], long PL lifetime [6] and marked size dependence of the PL maximum in the absence of toxic metals in the composition. To protect QDs from environmental influences and to improve PL and colloidal characteristics, a shell of a broader band semiconductor (ZnS) is applied on the surface of the ternary QD core. Among many methods for the synthesis of ternary core/shell QDs, the hot-injection method is used most effectively to control the QDs size and morphology due to the high temperature of synthe-

sis and the use of long-chain organic molecules as ligands [7–11]. However, organic long-chain ligands have hydrophobic properties that do not allow the synthesized QDs to be used in biological applications without the surface modification step [12]. Surface modification of colloidal QDs with short-chain multifunctional ligands such as 1-thioglycerol, thioglycolic acid, 3-mercaptopropionic acid, L-cysteine and glutathione ensures their stability in biomedical media and water [4]. Surface modification of colloidal QDs with such acids ensures their stability in biomedical media and water [4]. The nature and strength of the interaction between the surface ligands and QDs will determine the optical properties and stability of QDs [13]. Thio-group of the mercaptoacid molecules binds to the surface of the QD, and the carboxylic group exits into solution and creates a negative charge on the QD surface as a result of partial dissociation. Accordingly, methods for the direct synthesis of QDs in polar media, particularly water, have the advantages of milder synthesis conditions, the absence of an inert atmosphere and the absence of



organic solvent impurities [14]. Nevertheless, QDs obtained by aqueous methods often have less efficient optical properties [15, 16]. However, there are works in which hydrophilic ternary QDs with PL quantum yields (PL QY) up to 60–70% have been successfully obtained using mercaptoacids as surface ligands [17–21].

Despite the presence of a protective mercaptoacid layer, the large surface-to-volume ratio makes colloidal QDs sensitive to the environment [22]. Therefore using QDs as PL nanoobjects in bioapplications requires consideration of their behavior in biological environments, characterized by different pH and ionic strength. This encouraged us to study the effect of ionic strength and pH on the PL intensity and shape of spectra of different AIS/ZnS QDs capped with thioglycolic acid.

2. Experimental Section

2.1 Materials

All chemicals were of the highest purity commercially available and were used without further purification. Silver nitrate (AgNO_3 , 99.0%), indium chloride (InCl_3 , 99.9%), thioglycolic acid (TGA, 98.0%), sodium sulfide anhydrous (Na_2S , 90%+), ammonia solution (5 M), zinc (II) acetate anhydrous ($\text{Zn}(\text{CH}_3\text{COO})_2$), nitric acid (70%) were purchased from Sigma Aldrich (United States). Sodium chloride, hydrogen chloride and 2-propanol were received from Ekos-1 (Russia). The water used throughout this research was obtained by a Milli-Q water purification system (18.2 $\text{M}\Omega\text{-cm}$, Millipore, Germany).

2.2 Method of size-selected AIS/ZnS QDs preparation

Size-selected QDs capped with TGA were prepared according to the precipitation procedure described in the literature [23] (codenamed fractions #1–11). The molar ratio of precursors for the synthesis of QDs fractions was $\text{Ag} : \text{In} : \text{S} : \text{Zn} = 1 : 7 : 10 : 10$. For the investigation of the pH and ionic strength effects QD fractions, #2 QDs 605 ($\lambda_{\text{PL}} = 605 \text{ nm}$), #6 QDs 566 ($\lambda_{\text{PL}} = 566 \text{ nm}$) and #9 QDs 540 ($\lambda_{\text{PL}} = 540 \text{ nm}$) were adjusted to an optical density of 0.1 ($\lambda = 360 \text{ nm}$).

2.3 Protocol of the pH influence on the optical properties of AIS/ZnS QDs fractions studying

To vary pH, HCl (0.1 M) and NaOH (0.1 M) were added dropwise to 10 mL of QD fraction solutions until the desired pH values (range 2–12) were

reached. The effects of dilution and ionic strength can be neglected because these volumes are too small $< 0.1 \text{ mL}$ to significantly change the QDs concentration. A portion of 2 mL was placed in a cuvette to record absorption and PL spectra.

2.4 Protocol of the ionic strength influence on the optical properties of AIS/ZnS QDs fractions studying

For the investigation of the ionic strength, in the wells of the microplate, 50 μL of QDs were mixed with 50 μL of an aqueous solution of a sodium chloride with certain ionic strength to archive the ionic strength in final solution 0–1 M. Next, the PL spectra were recorded using a 96-well microplate reader.

2.5 Equipment

The synthesis of the AIS core and AIS/ZnS core/shell QDs was performed with automated synthesis system Atlas (Syrris, United Kingdom). Centrifuge 5430R Eppendorf with centrifuge bowl F-35-6-30 (radius 10.5 cm) (Germany) was used for purification and size-selective QDs precipitation. UV–VIS absorption spectra were recorded on a Shimadzu UV-1800 spectrometer (Shimadzu, Japan) in a standard 10-mm quartz cuvette. PL spectra of QDs were recorded by a fluorescence spectrophotometer Cary Eclipse (Agilent Technologies, Australia) in a 10-mm quartz cuvette. PL intensity for ionic strength analysis was recorded a BioTek Synergy H1 hybrid reader (BioTek Instruments Inc., United States) in a 96-well plate. The pH of the solutions was determined using an Ohaus a-AB33PH table pH meter (United States).

3. Results and Discussion

AIS/ZnS QDs were obtained using the solvent boiling point heating method. Silver nitrate – soft Lewis acid was used as an Ag^+ precursor, which interacted with the sulfhydryl group of thioglycolic acid to form a complex, resulting in a pale yellow solution. An ammonia solution was added to obtain a pH of 8–9 and the solution became colorless. InCl_3 (containing HNO_3), which is a strong Lewis acid [18], was used as an In^{3+} precursor. Na_2S was used as a sulphur source because of its direct solubility in water and high reactivity. When it was added, the reaction mixture turned bright yellow, which was the typical color of AIS formed by cation exchange. The solution was heated for half an hour at 96°C to form AIS nanocrystals. To protect the cores from



photodegradation and further enhance their PL properties, a shell of ZnS was grown in the second stage of synthesis by thermal decomposition of zinc thioglycolate at 96°C for half an hour.

It is worth noting that a feature of this synthesis technique is the wide distribution of QDs' size and properties, which requires a fractionation by size. The addition of 2-propanol to the obtained colloid of QDs caused their agglomeration due to the disturbance of electrostatic repulsion associated with the protonation of the ligand on the surface towards the uncharged form of COOH [24, 25]. This procedure resulted in 11 QDs fractions with the orange to green PL emission, as it is presented in Fig. 1. With increasing of fraction number, the size of QDs decreased, as evidenced by the shift of the absorption band edge towards low wavelengths in the absorption spectra and

the blue shift of the maximum of the PL band from 611 nm for fraction #1 to 527 for fraction #11 observed in the PL spectra. At the same time, the PL intensity was maximal for the intermediate fractions, which correlated with the PL QY and is consistent with the literature data [9].

For the *in vivo* application of these QDs it is important to evaluate the possible change in their properties due to the physiological environment. For a detailed study, we chose QD fractions with maximum color contrast: #2 QDs 605 (~3.5–4 nm); #6 QDs 566 (~3 nm), #9 QDs (~2 nm), from the original parent colloid [9], characteristics are given in Table 1.

Figure 2, *a* shows the effect of ionic strength on the PL intensity of selected QDs fractions by changing the NaCl concentration in the solution.

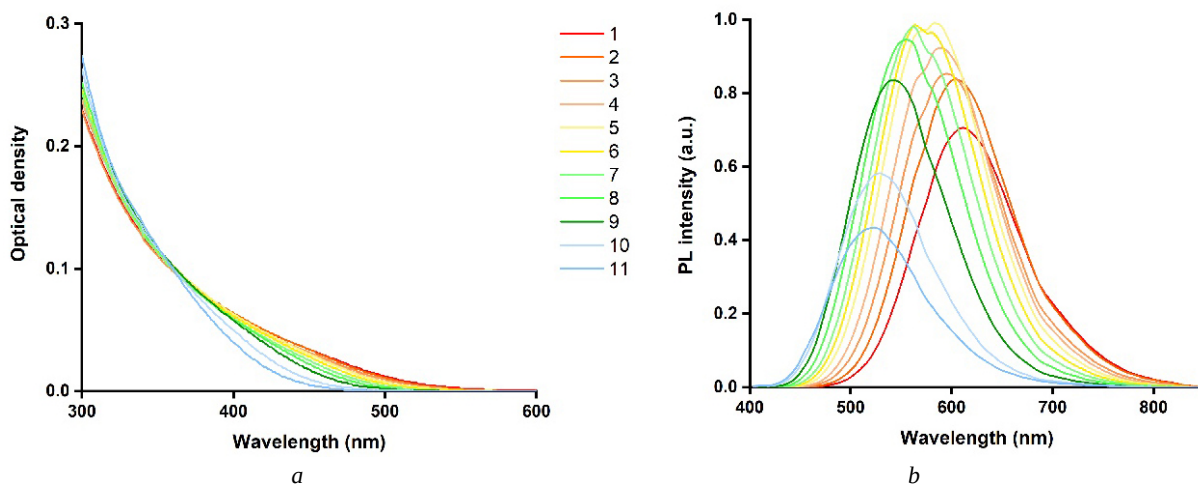


Fig. 1. Absorption (*a*) and PL (*b*) spectra of AIS/ZnS QDs fractions #1–11. Optical density of samples = 0.1; $\lambda = 360$ nm (color online)

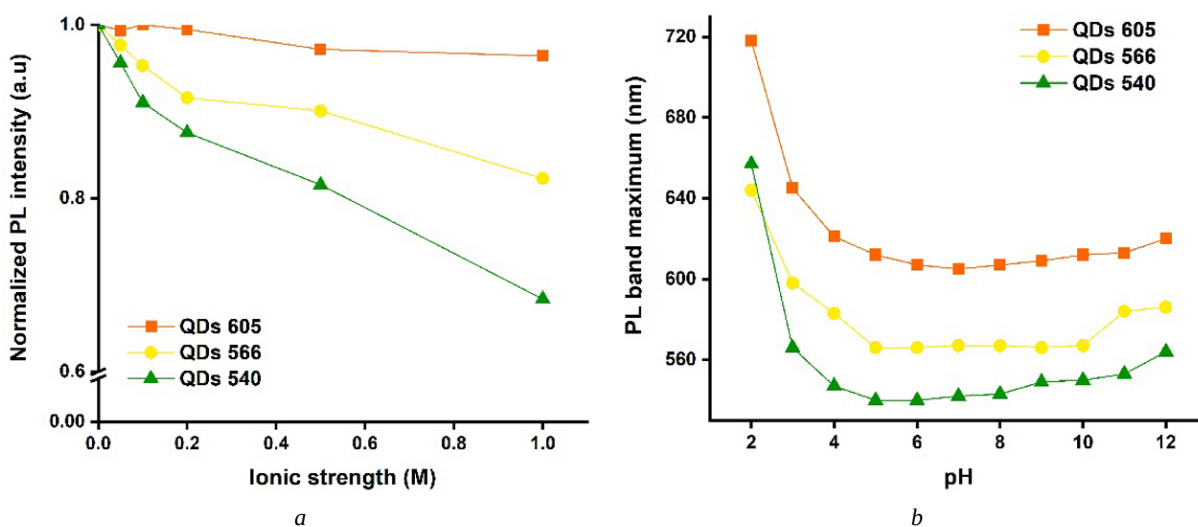


Fig. 2. Dependence of the normalized PL intensity of the QDs fractions on ionic strength (*a*) and dependence of the PL band maximum wavelength on pH (*b*) for the #2 QDs 605, #6 QDs 566 and #9 QDs 540 AIS/ZnS fractions (color online)



Table 1. Characteristics of selected AIS/ZnS QD fractions

Fraction number	λ_{PL} , nm	PL QY, %	Size [9]*, nm
#2	605	29	~3.5
#6	566	51	~3
#9	540	37	~2

* From high-resolution transmission electron microscopy.

As can be seen, decrease in the PL intensity of the QDs fractions was observed, as the ionic strength increased (Fig. 2, a). The position of the maximum of the PL peak does not change. Possibly, sodium cations form a cloud of counterions near the negatively charged surface of QDs and change the local electric field and the charge state of QD shell. These increase the probability of localization of the charge carrier on defects of nanocrystals and

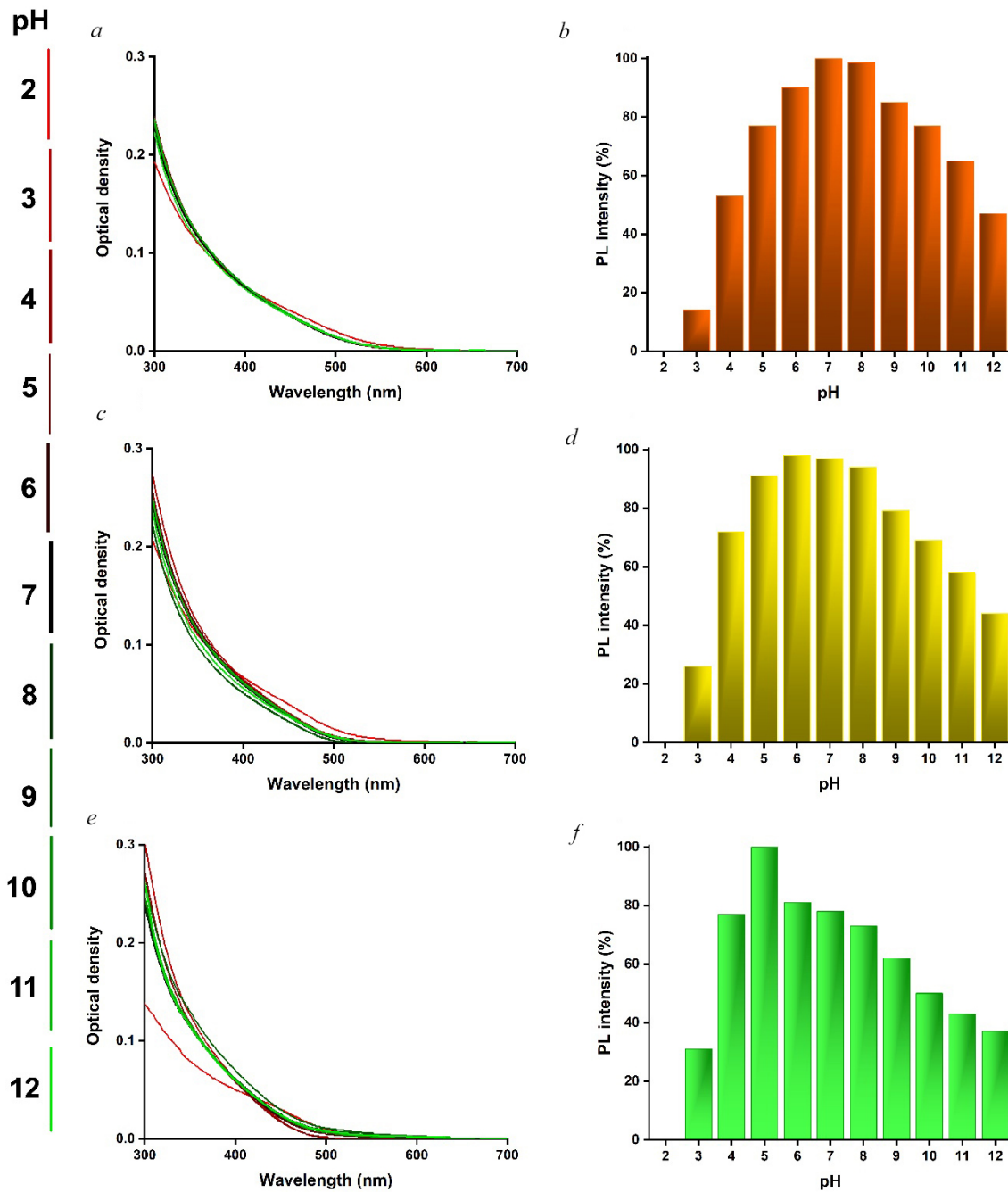


Fig. 3. Absorption spectra and PL intensity at different pH values for AIS/ZnS #2 QDs 605 (a and b), # 6 QDs 566 (c and d) and #9 QDs 540 (e and f) fractions. Optical density of samples = 0.1; $\lambda = 360$ nm (color online)



thus contributes to a decrease in the PL intensity. It should be noted that for all ionic strength values, the decrease in PL intensity is most pronounced for #9 QDs 540, and least pronounced for #2 QDs 605. Apparently, this effect is largely due to the amount of the TGA-layer and the number of defects in the lattice of the QDs. For #9 QDs 540, which are smaller compared to orange QDs, the contribution of surface defects is higher due to a larger surface-to-volume ratio and the amount of the TGA-layer is smaller. Nevertheless, under most applicable biological media, the ionic strength is 0.1–0.15 M, at which the PL intensity for all QDs fractions changes insignificantly (< 10%).

The effect of pH on the PL properties of the QDs fractions was evaluated by adding 0.1 M HCl and NaOH solutions. In a strongly acidic environment (pH = 2) in the absorption spectra of the #9 QDs 540 fraction solution the character of the curve changes reflect the formation of aggregates (Fig. 3, e). The appearance of aggregates with decreasing pH is probably due to the breakdown of the protective sheath on the QD surface. At intermediate pH values, the interaction between the QDs and the capping agent is apparently strong enough and the capping agent protects the QDs more effectively, so there are few changes in the absorption spectra. Similar phenomena in the absorption spectra were observed for #2 QDs 605 and #6 QDs 566 as shown in Fig. 3, a, b. However, it is worth noting that for the #9 QDs 540 fraction, the differences in absorption spectra in acidic medium were more pronounced than for #2 QDs 605 and #6 QDs 566. For #2 QDs 605 the PL intensity in acidic medium decreases more significantly than for #9 QDs 540 (Fig. 3, b, d, f). This is due to the inhibition of dissociation processes in an acidic environment (pH = 2–4), which decrease the negative charge on the QD surface. The more effective quenching of PL intensity in an acidic environment for #2 QDs 605 can be due to the presence of more TGA on the surface of #2 QDs 605 compared to #9 QDs 540. Whereas in an alkaline environment an inverse relationship is observed for #2 QDs 605. This is due to the deprotonation of the carboxyl group in alkaline medium (pH = 8–12), which creates electrostatic steric barriers and provides greater stability of QDs. In addition, a decrease in pH for all fractions of QDs resulted in a shift of the PL band maximum to the red region (Fig., 2 b). It should be noted here that in the pH range of 5–8 the red shift of the PL maximum was practically not observed, but at very low and high pH values the shift became noticeably large. These results indicate a sufficiently strong coordination bond between the ligands and QDs in the

pH range of 5–8. The retention of PL of QDs in the pH range corresponding to the physiological values of biological fluids demonstrates the advantages of using these QDs in bioanalysis and medicine.

Conclusions

In summary, we have reported the study of the PL properties of the ternary AIS/ZnS QDs fractions as a function of pH and ionic strength. In strongly acidic and strongly alkaline environments, a breakdown of the protective shell leading to structure and surface changes, as indicated by a shift of the PL maximum into the long-wave region and a strong drop in the PL intensity. The effect of reduced PL intensity at different ionic strengths was more pronounced for #9 QDs 540, indicating a greater contribution from surface defects due to the larger surface-to-volume ratio for the smaller QDs as well as a reduced stabilizing agent on the surface. Nevertheless, optical spectroscopy studies have shown that at intermediate pH levels, the PL intensity and the PL maximum undergo less change for the selected QD fractions. This suggests that the interaction between QDs and the capping agent is quite strong and that the capping agent protects QDs more effectively in the pH range that most corresponds to the physiological pH values of biological fluids.

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