Tuning the luminescence of thin nanocrystalline CsPbBr$_3$ perovskite films during the *in situ* anion exchange reaction

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Inorganic perovskite CsPbX$_3$ nanocrystals (PNCs), where X is a halide anion, are currently promising materials for a wide range of optoelectronic devices. One of the key tasks to be solved before they are used in practice is to obtain stable thin PNC films whose luminescence wavelength could be finely tuned. The chemical composition of CsPbX$_3$ PNCs is the main parameter determining their band gap width and, hence, the position of their photoluminescence maximum. Variation of the PNC composition in the course of their synthesis or postsynthetic treatment in solution makes it possible to obtain CsPbBr$_{(3-x)}$I$_x$ and CsPbBr$_{(3-y)}$Cl$_y$ materials emitting in the entire visible spectral range. In addition, these PNCs are more structurally stable than CsPbCl$_3$ and CsPbI$_3$ ones. However, most exchange reactions in solution reported in published studies are spontaneous and poorly controllable. In this study, the anion exchange reaction is proposed to be carried out directly on the formed thin film of CsPbBr$_3$ incorporated in the matrix of a copolymer of methyl and lauryl methacrylates. The exchange reactions with octadecylammonium iodide and PbI$_2$ leading to a shift of the photoluminescence maxima to longer wavelengths by 130 and 137 nm within 15 and 6 min, respectively. The study also shows the possibility of carrying out an ion exchange reaction on a substrate mimicking the real structure of a light-emitting diode.
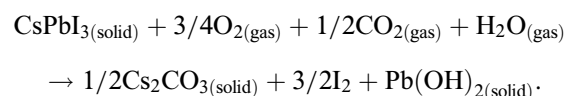
Keywords: inorganic perovskite nanocrystals, anion exchange, thin films, photoluminescence.

Introduction

Inorganic photoluminescent (PL) nanocrystals having the crystal structure of the perovskite mineral of the composition CsPbX$_3$, where X — halide anion, (PNC) combine a number of unique characteristics, such as high values of the quantum yield of luminescence (50−90%), intense light absorption in a wide UV and visible range, relative ease of synthesis, simple dispersion in various solvents and matrices (polymers, SiO$_2$, TiO$_2$, etc.) [1–5]. The position of the photoluminescence maximum of PNC CsPbX$_3$ can be controlled in almost entire visible spectral range. Besides, PNCs have a small full width of the PL maximum at half maximum (FWHM): about 12 nm in the blue region of the spectrum in the case of CsPbCl$_3$, about 20 nm in the green light wavelength range for CsPbBr$_3$, and 40−45 nm in the red region of the spectrum for CsPbI$_3$ [6]. These characteristics determine a wide range of prospects for the use of this class materials as components of solar cells, light-emitting diodes, photodetectors, displays, etc. [7–9]. The extraordinary interest of researchers in this area can be confirmed from the example of a rapid increase in the photoconversion efficiency of solar cells based on CsPbI$_3$ from 2.9% in 2015 to 21.0% in 2022 [10–12].

The forbidden band width (E_g) of PNC CsPbX$_3$ depends on the edge position of the conduction band formed by the overlap of 6s- and 6p-orbitals of Pb atoms, and the edge of the valence band, consisting of p-orbitals of halogen atoms. Thus, the spectral position of the PNC PL maximum directly depends on the chemical composition of the nanocrystals. Thus, for CsPbCl$_3$, CsPbBr$_3$, and CsPbI$_3$ the values E_g are 3.0, 2.36, and 1.74 eV, respectively [13,14]. PNCs based on cesium-lead iodides are the most promising in terms of application in solar cells [15], however, at the same time, they are the least thermodynamically stable in the series of compositions CsPbX$_3$ [16]. Besides, this type of PNC is more prone to degradation under the action of light, oxygen, and atmospheric moisture [13,17–19]. One of the possible options of PNC CsPbI$_3$ decomposition in air can proceed according to the reaction [16]:

$$CsPbI_{3(solid)} + 3/4O_{2(gas)} + 1/2CO_{2(gas)} + H_2O_{(gas)}$$

$$\rightarrow 1/2Cs_2CO_{3(solid)} + 3/2I_2 + Pb(OH)_{2(solid)}.$$

In addition to the chemical transformations described above, the phase transition of PNC CsPbI$_3$ from the black α-phase to the yellow nonperovskite δ-phase can also occur already at room temperature [20]. Thus, low stability is a serious obstacle to the successful introduction of PNCs

of this composition into optoelectronic devices and their commercialization. $CsPbBr_3$ nanocrystals are characterized by the highest stability of structural and optical properties, which is explained by the higher bond strength of $Pb-Br$ as compared to $Pb-I$, as well as by the higher value of the Goldschmidt correspondence factor for this composition (t) expressed by the formula (1) [13]:

$$t = \frac{r_{Cs} + r_{Pb}}{\sqrt{2}(r_{Pb} + r_X)}, \qquad (1)$$

where r_{Cs}, r_{Pb}, r_X — ionic radii of cesium, lead and the corresponding halogen. The closer the value t is to 1, the higher the stability of the structure of perovskite nanocrystals is. For PNC $CsPbX_3$ this value is in the range $0.7-0.9$ [21].

One of the ways to increase the stability of PNCs $CsPbI_3$ and $CsPbCl_3$ while maintaining the required optical and structural properties is the synthesis of PNCs with mixed composition and partial substitution of bromide ions for the required halogen. This becomes possible due to the low internal energy of the crystal lattice and the high concentration of vacancies, which leads to the instability of the structure, which manifests itself in the high mobility of halide ions. The literature shows successful examples of obtaining perovskite nanocrystals of composition $CsPbBr_{(3-x)}I_x$ and $CsPbBr_{(3-y)}Cl_y$ with PL maxima ranging from 410 up to 700 nm when carrying out ion exchange reactions with various halides both in solutions and through solid-phase reactions. [1,21,22]. Besides, cross anion exchange between PNCs of different compositions is also possible in the absence of an external source of halides [23]. In this case, the process of anion exchange in solution proceeds spontaneously and until compositional equilibrium is reached in the compositions of all individual nanocrystals present. Such reactions proceed at room temperature, however, they are significantly complicated by the low solubility of most of the halogen sources used for this purpose in organic solvents.

The key technological step in the creation of optoelectronic devices based on PNC is the formation of thin films (TF). At the same time, in the case of mixed-halogen materials obtained by anion exchange in solution, researchers encounter a number of difficulties in the manufacture of TF. For example, during the PNCs deposition in order to isolate them from the reaction mixture after ion exchange, concentration, and formation of the film itself, a significant drop in the intensity of the photoluminescence of the material occurs. In this paper we propose an approach to obtaining mixed-halogen PNCs by carrying out anion exchange reaction directly on a preliminarily formed thin film of $CsPbBr_3$ nanocrystals stabilized in a poly(lauryl-methyl methacrylate) (p(MMA-LMA)) matrix.

1. Experimental part

1.1. Synthesis of perovskite nanocrystals CsPbBr₃

Perovskite nanocrystals $CsPbBr_3$ were obtained by injection colloidal synthesis using $PbBr_2$ (99.999%, Aldrich) and cesium oleate as precursors in the $Cs:Pb$ mole ratio equal to $1:3.8$ [1]. Cesium oleate was obtained by the reaction of Cs_2CO_3 (99.9%, Aldrich) and oleic acid (98%, Aldrich) in 1-octadecene (90%, Sigma-Aldrich). The temperature of cesium oleate injection into a intensively stirred solution of lead oleate in octadecene was $180°C$. Isolation of PNCs from the reaction mixture and their purification from excess organic ligands was carried out by precipitation using methyl acetate (98%, Aldrich), followed by centrifugation at $12\,000$ rpm for 10 min, and redissolution in n-octane when treated in an ultrasonic bath. The quantum yield of luminescence of the obtained PNC sample was measured relative to the fluorescein dye according to the method described in [24].

1.2. Synthesis of p(MMA-LMA) copolymer

Synthesis of copolymer of lauryl methacrylate and methyl methacrylate in a molar ratio of $1:2$ was carried out by the method of radical polymerization in solution [25]. The methyl methacrylate monomer (99%, Aldrich) was preliminarily purified from the stabilizer by vacuum distillation, the lauryl methacrylate monomer (96%, Aldrich) was used without further purification. 1, 1'-azo(biscyclohexane carboniryl) (98%, Aldrich) was used as a thermal polymerization initiator. Solution polymerization was carried out at a temperature of $95°C$ in toluene, in an argon flow. The total concentration of monomers was 40% of weight of the solution, the mole fraction of the initiator was 0.5% relative to the monomers. The reaction was carried out for 8 h, after which the polymer solution was transferred into excess of methanol, the supernatant containing monomer residues was separated from the coagulated polymer, then the latter was dried in air at a temperature of $100°C$ for 2 h. The resulting polymer was dissolved in a given concentration of n-octane or toluene.

1.3. Production of thin films CsPbBr₃/p(MMA-LMA)

Thin films of $CsPbBr_3$/p(MMA-LMA) were deposited on borosilicate glasses 2.5×2.5 cm in size. The glass substrates were preliminarily cleaned by sequential treatment in a mixture of concentrated sulfuric acid and potassium dichromate for $15-20$ min, and in a mixture of concentrated nitric HNO_3 and hydrochloric HCl acids, taken in the ratio $1:3$ by volume, within $30-40$ min. Next, the cleaned glass substrates were washed with deionized water, after which they were dried in an oven at a temperature of $100-110°C$ for 2 h.
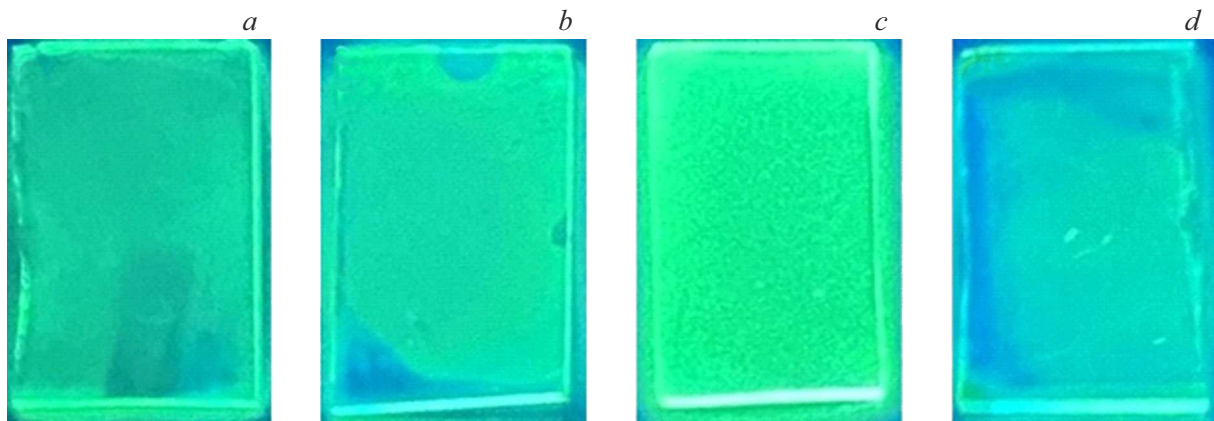
Figure 1. Thin films of CsPbBr$_3$/n(MMA-LMA) after treatment with solvents: tetrahydrofuran (*a*), acetonitrile (*b*), ethyl acetate (*c*) and ethanol (*d*).

To stabilize PNCs and to protect them from environmental effects (moisture, air, and light), an approach was implemented to deposit thin films from CsPbBr$_3$ solution and copolymer p(MMA-LMA) in octane. The mass fraction of the copolymer in the obtained samples with respect to PNC CsPbBr$_3$ was 25%.

The TF was fabricated by the rotating substrate method (spin-coating) on Spin-Coater KW-4A unit (Chemat). The substrates were mounted on a vacuum holder and 100 μl of the solution under study was applied to them. The films were formed at a rotation speed of 2000 rpm for 1 min, after which they were annealed on Ret Basic (IKA) plate at 70°C for 30 min to remove excessive solvent and relaxation of mechanical stresses in the film.

The fabrication of multilayer structures imitating the structure of LEDs based on PNC was carried out according to the following procedure. Glass substrates with a layer of indium-tin oxide (ITO) were preliminarily cleaned by treatment in an ultrasonic bath in various solvents (isopropanol, deionized water), and then subjected to treatment in oxygen plasma. Next, on substrates a hole-injecting layer PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrenesulfonate) was deposited by spin-coating at 2000 rpm followed by annealing at 110°C for 10 min. PEDOT:PSS film thickness was 30−35 nm (film thicknesses were determined using an MII-4 microinterferometer). Substrates coated with PEDOT:PSS layer were transferred to a glove box with an argon atmosphere (O$_2$ < 1 ppm, H$_2$O < 1 ppm). Next, on substrates hole transport layers poly-TPD (poly(N,N′-bis-4-butylphenyl-N,N′-bisphenyl)benzidine were applied, from a solution in chlorobenzene, 8 μg/μl) and PVK (poly(vinylcarbazole), from solution in o-xylene, 1.5 μg/μl) by spin-coating at 2000 rpm. Poly-TPD (30 nm) and PVK (5 nm) layers were annealed at 100°C for 10 min before deposition of the last light-emitting layer based on PNC. PNC films in pure form or as part of a polymer composite with different content of p(MMA-LMA) were deposited by spin-coating varying the process parameters and solution composition, after which the fabricated structures were annealed at 100°C for 10 min.

1.4. Manufacture of halide precursors for ion exchange

In this paper saturated solutions of PbI$_2$ (99.999%, Aldrich) and octadecylammonium iodide (ODA-I) were used as sources of iodide ions. The latter was obtained in the reaction between octadecylamine (99%, Aldrich) and HI (57% aqueous solution, Aldrich) with stirring on a magnetic stirrer in ethanol for 2 h [22].

Before carrying out experiments on ion exchange, the most suitable solvent for carrying out the anion exchange reaction was selected. To do this, the substrates with the formed TF CsPbBr$_3$/p(MMA-LMA) were immersed in solvents with different polarity, including tetrahydrofuran, ethyl acetate, acetonitrile, ethanol, chlorobenzene, and methyl acetate, followed by visual inspection of changes in the brightness and integrity of the films. As a result of the experiments, ethyl acetate was chosen as the solvent for *in situ* ion exchange (Fig. 1).

ODA-I and PbI$_2$ solutions of the same halogen molarity were obtained by dissolving the calculated amounts of salts in ethyl acetate under ultrasound action for 50 min.

Ion exchange reactions were carried out by adding droplets of ODA-I and PbI$_2$ solutions to crystallizers, where TF CsPbBr$_3$/p(MMA-LMA) and of 2 μl pure ethyl acetate were placed beforehand. Experiments were carried out at room temperature; during the ion exchange the photoluminescence spectra were recorded *in situ* using a fiber optic probe connected to a CaryEclipse (Agilent) spectrofluorimeter. Similar experiments were also carried out with CsPbBr$_3$/p(MMA-LMA) films deposited on substrates imitating the real LED structure (ITO/PEDOT:PSS/poly-TPD/PVK).
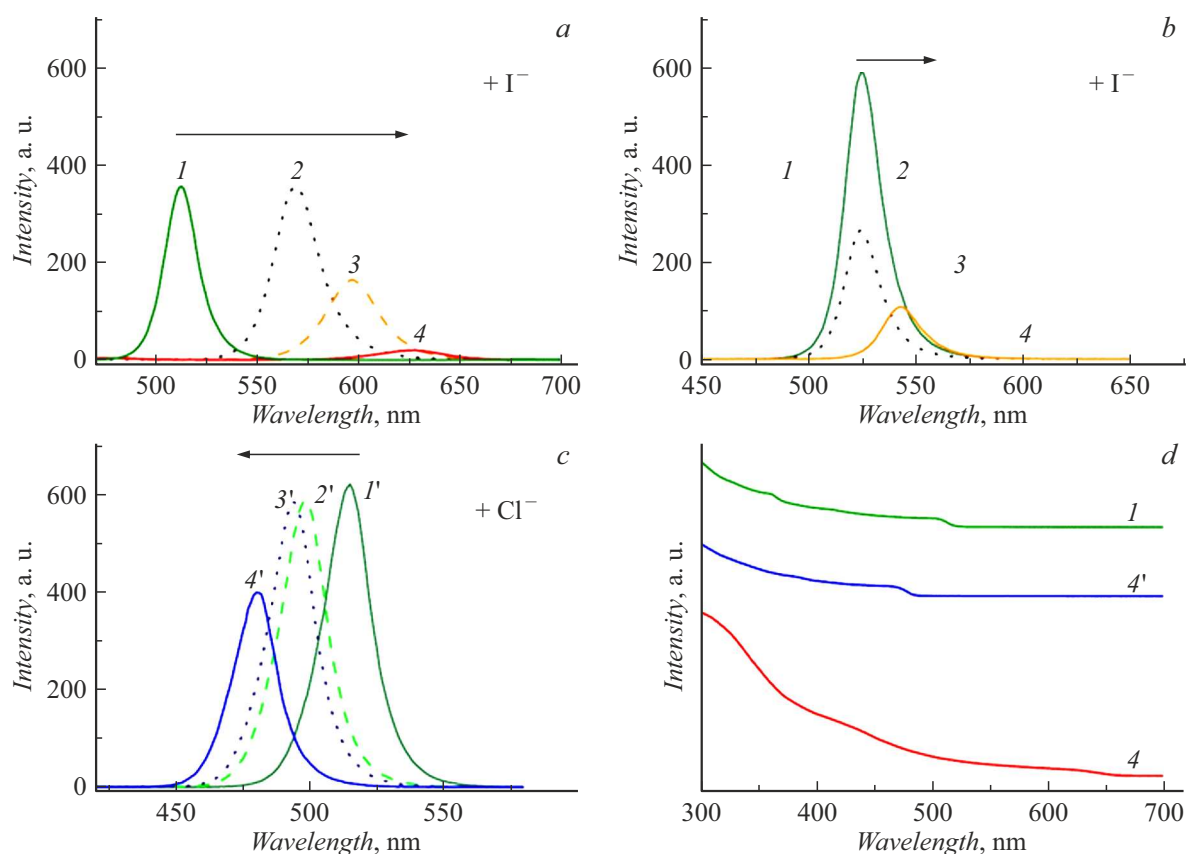
Figure 2. Dynamics of change in position of the maximum of the photoluminescence spectrum during the anion exchange reaction in solution between PNC $CsPbBr_3$ and ODA-I (*a*), PbI_2 (*b*), $PbCl_2$ (*c*); absorption spectra of PNC $CsPbBr_3$ (*1*), $CsPbBr_{(3-x)}I_x$ (*4*) and $CsPbBr_{(3-y)}Cl_y$ (*4'*) (*d*). The numbers denote the PNC compositions with different degrees of substitution of bromide ions, aliquots of which were taken at the reaction time intervals indicated in Table 1.

Table 1. Dynamics of changes in the optical properties of mixed-halogen PNCs obtained by the anion exchange reaction in solution between and ODA-I in the case of $CsPbBr_{(3-x)}I_x$ and $PbCl_2$ in case of $CsPbBr_{(3-y)}Cl_y$

Sample	$CsPbBr_3$ (*1*)	Anion exchange with ODA-I			Anion exchange with $PbCl_2$		
		2	*3*	*4*	*2'*	*3'*	*4'*
λ_{max}, nm	513	569	597	628	498	494	481
FWHM, nm	20.2	26.0	30.4	38.5	20.5	20.2	19.7
t, min	0	7	13	17	120	150	180

2. Results and discussion

The fabricated $CsPbBr_3$ perovskite nanocrystals are characterized by a rather high quantum yield of PL equal to 67%, and a moderate degree of ensemble monodispersity in size, as it is confirmed by the small width of the luminescence maximum at half maximum (18.4−20.2 nm) for all fabricated samples of PNC. The first experiments on partial replacement of PNC $CsPbBr_3$ bromide ions with iodine were carried out in solution. To do this, the calculated amounts of ODA-I, as well as lead iodide and chloride were added to solution containing a known

amount of nanocrystals, and it was intensively stirred at room temperature. To monitor the depth of the reaction at different time intervals, aliquots 20 μl were taken from the solution (Fig. 2), and their spectral characteristics were studied. The dynamics of changes in the optical properties of PNC during ion exchange in solution (maxima in the luminescence spectra, full width of the photoluminescence peak at half maximum) is presented in Table 1. As a result of the experiment, it was found that in the case of the reaction with ODA-I, the shift in the position of the PNC $CsPbBr_3$ emission maximum to the long-wavelength region of the spectrum was 115 nm for 17 min (Fig. 2, *a*,
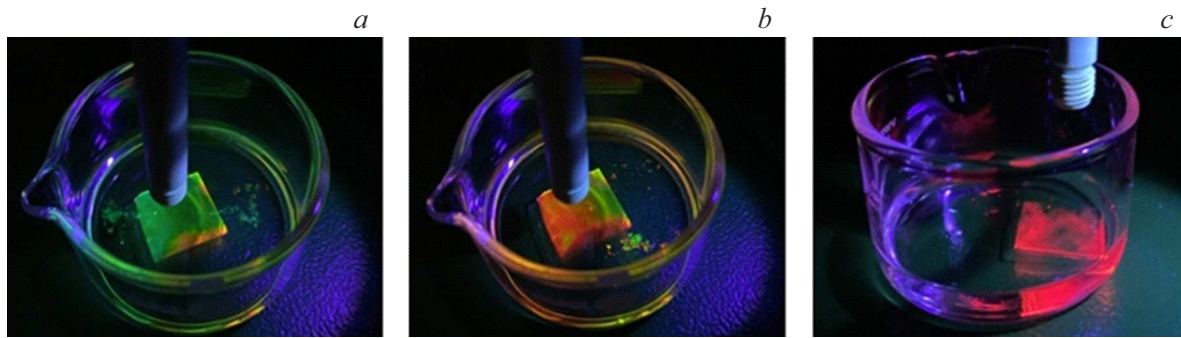
Figure 3. Initial thin film CsPbBr$_3$/p(MMA-LMA) (*a*), reaction of anion exchange with ODA-I (*b*) and PbI$_2$ (*c*).

Table 2. Dynamics of changes in the optical properties of CsPbBr$_3$/p(MMA-LMA) thin films during the reaction of anion exchange with PbI$_2$ *in situ*

PNC	CsPbBr$_3$ (*1*)	*2*	*3*	*4*
λ_{max}, nm	513	517	625	650
FWHM, nm	18.9	24.6	68.4	43.4
t, min	0	2	4	6

Table 3. Dynamics of changes in the optical properties of CsPbBr$_3$/p(MMA-LMA) thin films during the reaction of anion exchange with ODA-I *in situ*

PNC	CsPbBr$_3$ (*1′*)	*2′*	*3′*	*4′*	*5′*	*6′*
λ_{max}, nm	513	523	587	613	619	643
FWHM, nm	18.4	34.5	51.5	49.2	39.6	38.5
t, min	0	1	3	5	10	15

Table 1). However, there was a significant decrease in the photoluminescence intensity of the sample to a value comparable with PNC CsPbI$_3$ synthesized by the classical direct method. The reaction with lead iodide proceeds much more slowly. So, for 48 h offset λ_{max} of PL into the red region occurred only by 30 nm (Fig. 2, *b*). This can be explained by the lower solubility of PbI$_2$ in organic solvents compared to octadecylammonium iodide. The reaction of anion exchange with lead chloride led to a shift in the position of the photoluminescence maximum to the short wavelength region by 32 nm per 3 h (Fig. 2, *c*, Table 1). In this case, the quantum yield of PL of PNC decreased to 37%. The formation of PNCs with the compositions CsPbBr$_{(3-x)}$I$_x$ and CsPbBr$_{(3-y)}$Cl$_y$ is also accompanied by a change in the full width of the photoluminescence maxima at half maximum (Table 1).

The anion exchange reaction carried out by dropping solutions of ODA-I and lead iodide in ethyl acetate directly onto the formed thin film of CsPbBr$_3$/p(MMA-LMA)

(Fig. 3) proceeds much faster (Table 2, 3). For example, when TF CsPbBr$_3$/p(MMA-LMA) was treated with PbI$_2$ solution, λ_{max} shift to the red region by 137 nm occurred for 6 min only (Table 2, Fig. 4, *a*), however, the integrated PL intensity decreased by 9.7 times. When carrying out the reaction with ODA-I, the shift of the maximum of the PL spectrum was 130 nm for 15 min (Table 3, occurred to a much lesser extent — by 4.6 times. At the same time, having estimated the degree of symmetry of the photoluminescence maxima, one can make an assumption about a faster equilibrium of the anion exchange reaction I$^-$ ↔ Br$^-$ in the reaction with ODA-I.

In the photoluminescence spectra of the intermediate states and products of the ion exchange reaction of TF CsPbBr$_3$/p(MMA-LMA) with PbI$_2$ (*3* and *4* in Fig. 4, *a*) and ODA-I (*3′−6′* in Fig. 4, *b*) additional peaks of very low intensity occur. The appearance of such additional peaks can be explained by the presence of two reaction stages in the anion exchange process: diffusion of iodide ions in solution to the surface of PNC, and their diffusion already in the solid phase of perovskite nanocrystals [26]. Apparently, this leads to local differences in the degree of substitution of bromide ions in perovskite nanocrystals and externally affects the shape of the spectral line.

Based on the results of primary studies for conducting experiments with CsPbBr$_3$/p(MMA-LMA) films deposited on multilayer substrate that imitates the structure of LED (ITO/PEDOT:PSS/poly-TPD/PVK), as a source iodide ions, ODA-I was chosen for the anion substitution reaction. The results of the experiment are shown in Fig. 5 and Table 4. The proposed method for manipulating the spectral characteristics of a light-emitting layer based on PNC turned out to be highly effective: for 1 min the shift of the PL maximum to the red region of the spectrum was 90 nm, while maintaining high emission intensity.

Summing up the obtained results, we can conclude that the anion exchange reaction can be carried out directly on the formed thin films of PNC CsPbBr$_3$, which greatly simplifies the rearrangement of the forbidden band and the photoluminescence spectral region of this class of nanomaterials. The developed approach makes it possible to efficiently carry out a controlled change in the luminescence
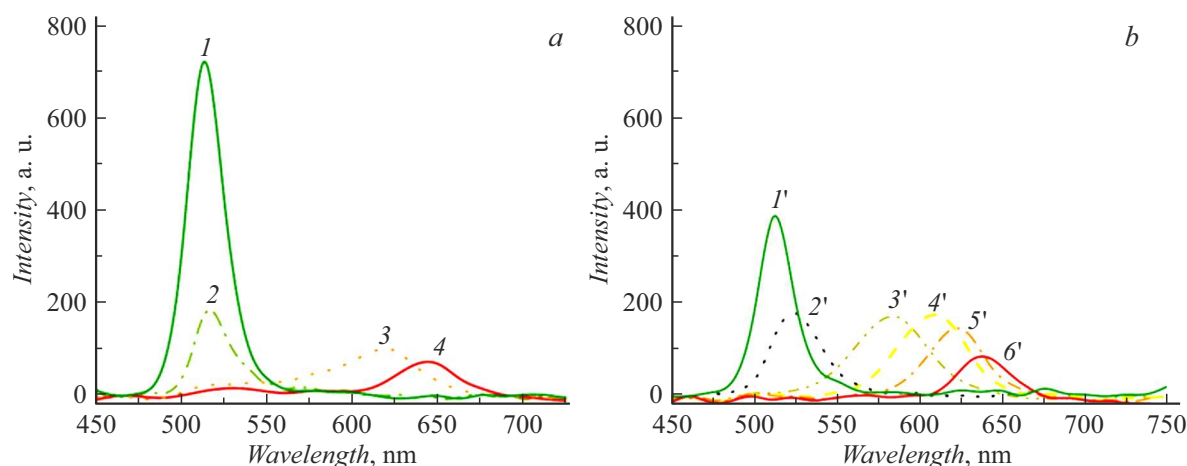
Figure 4. Dynamics of change in the position of the maximum of the photoluminescence spectrum during the anion exchange reaction on thin films CsPbBr$_3$/n(MMA-LMA) with PbI$_2$ (*a*) and ODA-I (*b*). The numbers indicate the spectra at different times of the reaction, corresponding to the compositions of PNC with different degrees of substitution of bromide ions.
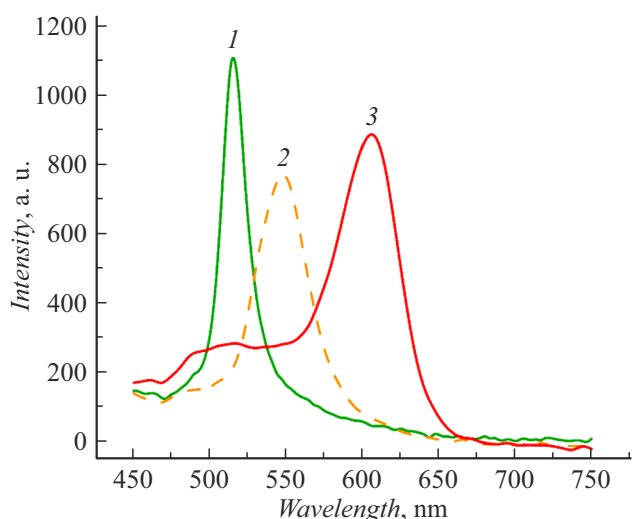

Figure 5. Change in the photoluminescence spectra of CsPbBr$_3$/p(MMA-LMA) multilayer structures on substrate ITO/PEDOT:PSS/poly-TPD/PVK as a result of anion exchange with ODA-I after 0 (*1*), 30 (*2*) and 60 (*3*) s.

Table 4. Dynamics of changes in the optical properties of CsPbBr$_3$/p(MMA-LMA) multilayer structures on substrate ITO/PEDOT:PSS/poly-TPD/PVK during reaction of anion exchange with ODA-I *in situ*

PNC	CsPbBr$_3$ (*1*)	*2*	*3*
λ_{max}, nm	513	548	603
FWHM, nm	21.2	42.5	53.6
t, s	0	30	60

properties of PNC TFs in a wide range of the visible spectrum and, in the future, can solve the problem of maintaining the stability of their structural and optical properties, which is one of the key problems of further PNC integration into optoelectronic devices. The successful example of carrying out the anion exchange reaction on PNC TFs deposited on actual multilayer LED structure shown in this paper opens up the prospect of optimizing the entire process of manufacturing optoelectronic devices with specified optical characteristics.

Conclusion

As a result of the study, the possibility and prospects of using the method of changing the spectral characteristics of thin films of perovskite nanocrystals CsPbBr$_3$ stabilized in p(MMA-LMA) polymer matrix by carrying out the anion exchange reaction *in situ* at room temperature are shown. This approach has a number of advantages over the fabrication of mixed-halogen PNCs by anion exchange in solution, including a significantly higher reaction rate with a small drop in photoluminescence intensity, as well as absence during fabrication of steps of PNC CsPbBr$_{(3-x)}$I$_x$ isolation from the reaction medium and their concentration. The result of the paper was a demonstration of the possibility of rearranging the photoluminescence spectrum of thin composite films CsPbBr$_3$/p(MMA-LMA) using solutions of ODA-I and PbI$_2$ in ethyl acetate as sources of iodide ions. The best quality of thin films was achieved in the first case, while the shift of the PL spectrum to the red region as a result of ion exchange was 130 nm for 15 min. The results obtained made it possible to demonstrate the possibility of carrying out ion exchange directly in multilayer structures simulating a real LED. The developed methods can become the basis for further studies aimed at the controlled shift of the photoluminescence spectrum of thin PNC films to the

blue region of the spectrum, and, accordingly, obtaining potentially promising materials for the development of energy-saving light-emitting diodes with a white emission spectrum.

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Conflict of interest

The authors declare that they have no conflict of interest.

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