

Chiral properties of quasi-two-dimensional S-BPEA-based perovskites

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Efficient, miniaturized and well-scalable optical radiation detectors sensitive to light with left and right circular polarization are required for successful integration of technologies based on the use of circularly polarized radiation. A key aspect of the development of photodetectors of this class is the development of new chiral photoactive layers. This paper presents a protocol for the synthesis of a new optically active quasi-two-dimensional organo-inorganic perovskite based on the chiral molecule S-(4-bromophenyl)ethylamine. The photovoltaic and chiroptic properties of the obtained quasi-two-dimensional perovskites are investigated, as well as the morphology of their surface is analyzed. It is shown that the presence of an additional bromine atom in the chiral molecule increases the photoconductivity of a film based on chiral perovskite by an order of magnitude, and the formation of a mixed anionic composition in quasi-two-dimensional perovskite significantly increases the absorption dissymmetry factor, which reaches a value of $3.3 \cdot 10^{-4}$.

Keywords: perovskite, chirality, circular dichroism, thin films.

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Introduction

Detection of circularly polarized radiation (CPR) is an important technology, which is widely used in spintronics [1], medical technology, transmission and encryption of information, design of optical radars [2,3], quantum optics and quantum communications [4,5], and also magnetic recording of information [6]. Modern systems of CPR detection are often based on complexes of optical elements — quarter-wave plates, polarization filters and complex interferential modules, which require precise positioning of components, are not vibrationally stable, and have large dimensions. Therefore, it is necessary to search for the methods to solve this problem in the form of development of highly sensitive modular devices devoid of faults of existing solutions.

Optoelectronic properties of nanomaterials with the structure of perovskite makes them a promising material for the design of the devices of direct detection of light with the left (L) and right (R) circular polarization [7]. Quasi-two-dimensional perovskites are most suitable materials for the development of such devices in virtue of relative simplicity of their production (including with the possibility of scaling to larger areas) and availability of a photo response in a wide optical range (from shallow UV to near IR). The general formula of such quasi-2D-perovskites is expressed as $(A_1)_2(A_2)_{n-1}(Pb)_nX_{3n+1}$ or $(A_1)(A_2)_{n-1}Pb_nX_{3n+1}$, where A_1 — large univalent or bivalent cation, A_2 — univalent cation of small size, and X — halogen. The number of inorganic layers, n , varies from 1 (pure 2D-structure) to ∞ (3D-structure), besides, the intermediate values

($n = 2-5$) correspond to quasi-two-dimensional (quasi-2D) perovskites [8]. Induction of chirality in quasi-2D-perovskites is usually achieved by using molecules of R-/S-methylbenzylamine (R-/S-MBA) and/or (R/S) — (1-(1-naphthyl)ethylamine) ((R/S)-1-NEA) [9,10] as cation A_1 , which makes it possible to achieve the factors of absorption dissymmetry (g_{abs}) above $4 \cdot 10^{-3}$. However, use of large chiral cations, which are located between the layers of halogenide-lead octahedrons considerably reduces the efficiency of charge transfer in the perovskite film, which causes deterioration in the efficiency of detection of radiation in the end device [11]. Therefore, the development of quasi-2D perovskites that combine the high factors of dissymmetry and effective transport of charge carriers is a relevant scientific problem. It was reported that introduction of achiral quasi-2D perovskites of cations based on 2-(4-bromophenyl)ethylamine (BPEA) in the composition improves the stability and interlayer charge transfer due to the coupled structure of the molecule [12], besides, it was demonstrated that it was possible to create a chiral perovskite based on this molecule [13]. Use of chiral enantiomers of molecules with the coupled structure for the formation of a photoactive layer of selective CPR detectors on the basis of quasi-2D perovskites may improve the operating characteristics of the obtained devices. For this purpose it is necessary to develop new protocols for synthesis of quasi-2D-perovskite films and for study of their optical and morphological properties.

This paper presents the protocol to form quasi-2D-perovskite films on the basis of halogenide salt of the molecule of 2-(4-bromophenyl)ethylamine (S-BPEAX,

Table 1. Molar ratios of MAI to chiral salt and mass of reagents used for synthesis

Molar ratio MAI to chiral salt	MAI, mg	PbI ₂ , mg	Chiral salts, mg	
			S-BPEABr	S-BPEAI
1:0	9.5	18.4	0.0	0.0
5:1	7.9		2.8	3.3
2:1	6.3		5.6	6.5
1:1	4.8		8.4	9.8
1:2	3.2		11.3	13.1
1:5	1.6		14.1	16.4
0:1	0.0		16.9	19.6

where X = Br, I). It is shown that the presence of the additional bromine atom in the S-BPEA molecule compared to the reference S-MBA molecule provides significant influence at photoelectric properties of the perovskite films. Changes were demonstrated in the spectra of circular dichroism of perovskite films from the quantity of the chiral cation and type of halogen in the salt of the chiral molecule (S-BPEAX) used for perovskite synthesis. It is shown that the increase in the quantity of the chiral cation causes deterioration of the morphology of the film surface.

Methods

Synthesis of chiral salts

1 mL S-BPEA or S-MBA were mixed with 3 mL of ethanol. Then the obtained mixtures were placed in an ice bath, and drops of hydrobromic acid (HBr) was added to them with vigorous mixing in the quantity providing for molar ratio of amine to acid 1:1. After addition of acid, the solution was mixed for 12 h. Upon expiration of the specified time, the solution was evaporated at temperature 80–100 °C to produce yellow crystals. The produced crystals were flushed 3–5 times with diethyl ether until crystals were bleached, and then the mix was dried by method of lyophilization (BK-FD10P, BIOBASE, KHP) for 12 h.

Formation of quasi-2D-films of chiral perovskites

Methyl ammonium iodide (MAI), chiral salt of bromine or iodine and PbI₂ were mixed with 150 μL dimethylsulfoxide (DMSO; the quantity was estimated based on 1 M concentration of PbI₂ in DMSO) at molar ratio of cation A to cation B, equal to 3:2, and were mixed for an hour at temperature 60 °C. Then the solution was filtered via a hydrophobic filter from polytetrafluorethylene (PTFE) with pore dimensions of 0.22 μm. Perovskites based on BPEAX

were also synthesized with different ratios of MAI/BPEAX, ratios of precursors used in various syntheses are presented in Table 1. Bases on the stoichiometric ratio of precursors, the suggested chemical formula of the produced perovskite is A₂PbX₇ (A — MAI/S-BPEAI or MAI/S-BPEABr, X — I or Br).

Perovskite films were formed with the help of application onto the rotary substrate (spin-coating). The previously cleaned glass substrate was coated with 50 μL of the solution filtered via a PTFE-filter (pore size 0.45 μL), and then the substrate was spun at speed of 5000 RPM for 40 s with acceleration of 1000 RP(S)². At the 15th second of spinning, 150 μL of chlorobenzene were added, which serves as an anti-solvent. Then substrates were annealed for 10 min at temperature of 100 °C.

Characterization of films

Spectra of circular dichroism (CD) were measured using a spectrophotometer J-1500 (Jasco, Japan). The absorption dissymmetry factor g_{abs} was assessed using formula (1) [14]:

$$g_{\text{abs}} = \frac{D_L - D_R}{D} = \frac{\theta[\text{mdeg}]}{32980D}, \quad (1)$$

where θ [mdeg] — intensity of CD signal, D_L and D_R — optical density accordingly at the left and right circular polarization of incident radiation, D — optical density for non-polarized light.

The morphology of film surface was studied using an atomic force microscope (AFM) Solver-Pro M (NT-MDT, Russia).

Photoconductivity study

To study the photoconductivity of chiral quasi-2D-perovskites, the planar architecture ITO/perovskite/Ag was used. The substrate was glass with a transparent conducting ITO layer, onto which the layer of chiral perovskite was applied. Silver electrodes with thickness of 100 nm were applied on the surface of the active layer by the method of thermal vacuum sputtering.

Photoinduced currents were recorded when illuminated with a laser with a wavelength of 405 nm and power density of 14 μW/cm². Light and dark currents were measured using a picoammeter (2636B, Keithley, USA) when the shift voltage changes in the range from –1 to +1 V. The photoinduced current density was determined using formula (2)

$$J_{\text{ph}} = \frac{I_{\text{light}} - I_{\text{dark}}}{S}, \quad (2)$$

where I_{light} — current measured under laser flash, I_{dark} — dark current, S — area of photoactive site (0.33 cm²). Specific photoconductivity of the layer (σ_{ph}) and vertical specific conductivity of the layer ($\sigma_{\text{ph}}^{\text{d}}$) were calculated using formulae (3) and (4) accordingly

$$\sigma_{\text{ph}} = \frac{I_{\text{light}} - I_{\text{dark}}}{S \cdot V}, \quad (3)$$

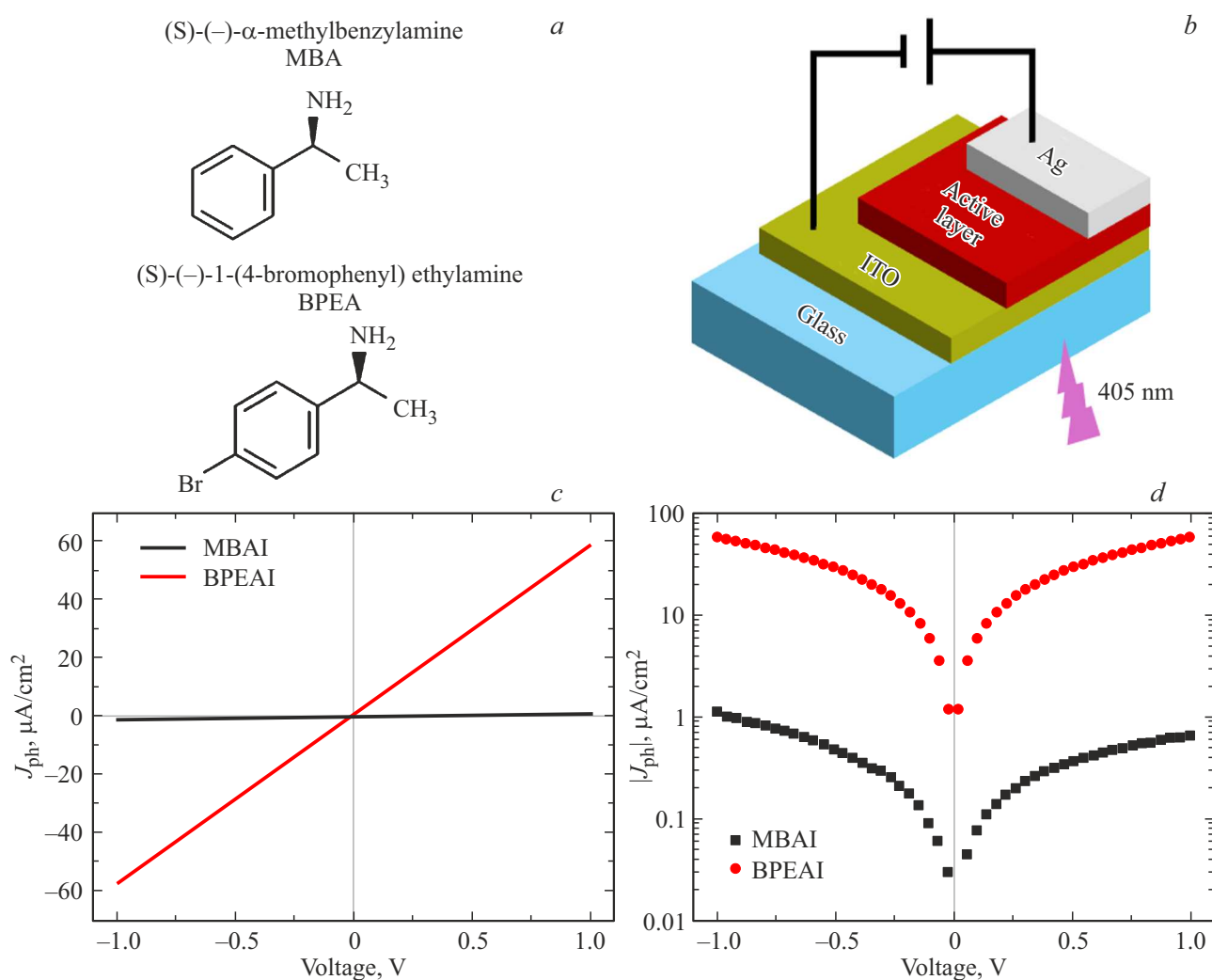


Figure 1. Structural formulas of S-MBA and S-BPEA molecules (a); device architecture for measurement of photoconductivity (b); dependences of density of photoinduced current J_{ph} of perovskite films based on S-MBAI (black) and S-BPEAI (red) at the linear (c) and logarithmic (d) scales.

$$\sigma_{\text{ph}}^{\text{d}} = \frac{(I_{\text{light}} - I_{\text{dark}})d}{SV}, \quad (4)$$

where V — shift voltage, d — layer thickness.

Results

To establish the influence of the additional bromine atom in the chiral molecule (structures of the corresponding molecules are shown in Fig. 1,a) at the conductivity of the obtained quasi-2D perovskites, planar structures were formed to measure the vertical photoconductivity (Fig. 1,b). Fig. 1,c,d presents the dependences of the density of photoinduced current J_{ph} on the applied voltage V for chiral quasi-2D-perovskite structures containing chiral BPEAI (red lines) and MBAI (black lines) cations. The MBA molecule was chosen as a reference sample in virtue of its identity with the BPEA molecule, except for the substitution of one

hydrogen atom with the bromine atom in a benzene ring with preservation of their chiroptic characteristics.

For the structure based on BPEAI with application of voltage from -1 to $+1$ V the density of current changes linearly from -57.3 to $58.5 \mu\text{A}/\text{cm}^2$. Besides, the shape of volt-ampere characteristic is symmetrical relative to zero shift voltage, which is a sign of symmetrical conductivity. For the structure based on MBAI in the similar process of measurement the recorded currents are lower by two orders of magnitude: from -1.1 to $1 \mu\text{A}/\text{cm}^2$. Note also that when MBAI is used, the dependence is not symmetrical (Fig. 1,d), with higher current under negative shift voltage. Specific photoconductivity was $8.8 \cdot 10^{-5} \text{ S}/\text{cm}^2$ for BPEAI and $8.6 \cdot 10^{-7} \text{ S}/\text{cm}^2$ for MBAI. A more informative value for the comparison of two materials is the vertical specific photoconductivity (σ_{ph}), making it possible to account for the layer thickness. Layer thicknesses were 52 nm and 100 nm for the samples

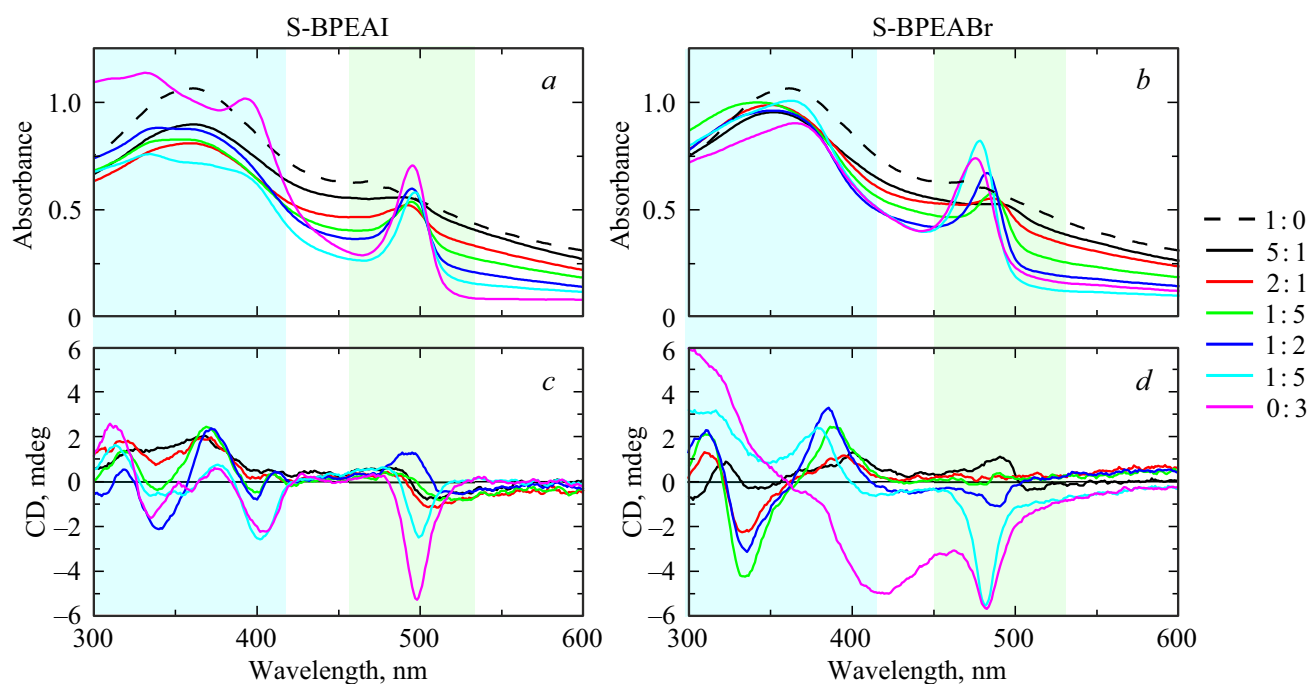


Figure 2. Spectra of optical density (*a,b*) and circular dichroism (*c,d*) of S-BPEAI (*a,c*) and S-BPEABr (*b,d*) perovskites with different molar ratio of chiral and achiral cation.

with BPEAI and MBAI accordingly. For the structure containing BPEAI, σ_{ph} was $(300 \pm 3) \cdot 10^{-12}$ S/cm, whereas for the sample with MBAI — $(8.6 \pm 1.6) \cdot 10^{-12}$ S/cm. From the obtained values it follows that the presence of the additional bromine atom in the molecule structure improves the photoconductivity of the chiral quasi-2D-perovskite on its basis, which may be the result of higher concentration of charge carriers or elevated mobility of the charge carriers.

To develop the effective devices with the selective response to CPR, it is also necessary to achieve the maximum values of the factor of absorption dissymmetry, and also to establish the influence of the ratio of chiral/achiral cation at the value of the factor of dissymmetry. Additionally it is necessary to investigate the possibility to shift the position of the absorption bands, where the circular dichroism is observed. For this purpose the samples of quasi-2D-perovskites were created with different ratios of chiral and achiral cations (Table 1). Instead of chiral salt S-BPEAI, S-BPEABr was also used for partial substitution of iodine with bromine in the crystalline lattice of perovskite [15]. Besides, the molar ratio of organic precursors (MAI and S-BPEAX together) to PbI_2 remained unchanged. Further this paper will only consider the change of the molar ratio MAI to S-BPEAX.

For the films produced using various molar ratios of chiral and achiral precursors (MAI/S-BPEAX), the spectra of absorption and CD were measured (Fig. 2). CD signals in the absorption of these films may be divided into two groups: one in the range of 300–450 nm, the second one

Table 2. Coefficients of absorption dissymmetry and roughness of film surface at different molar ratios of chiral and achiral cations

Molar ratio MAI/S-BPEAX	Coefficients of dissymmetry, 10^{-4}		Roughness of surface, nm	
	S-BPEABr	S-BPEAI	S-BPEABr	S-BPEAI
1:0	—	—	29 ± 3	
5:1	-0.21 ± 0.05	0.45 ± 0.05	10 ± 2	16 ± 3
2:1	~ 0	0.85 ± 0.05	6 ± 2	8 ± 2
1:1	~ 0	0.78 ± 0.05	7 ± 2	14 ± 2
1:2	0.78 ± 0.05	0.81 ± 0.05	15 ± 3	11 ± 2
1:5	2.3 ± 0.1	1.1 ± 0.1	20 ± 3	14 ± 3
0:1	3.3 ± 0.1	2.2 ± 0.1	25 ± 3	15 ± 3

— in the range of 480–500 nm. CD signals in the range of wavelengths 300–450 nm arise for certain different reasons, with the main ones being the following — interaction of the perovskite matrix with the molecule and structural deformations of the film [16] (which is confirmed by the result of the surface morphology analysis further). The detailed analysis of CD in this area is beyond this paper.

In the range of 480–500 nm the absorption spectrum shows a transition occurring in virtue of the quantum limitation effect in the quasi-two-dimensional perovskites [17,18].

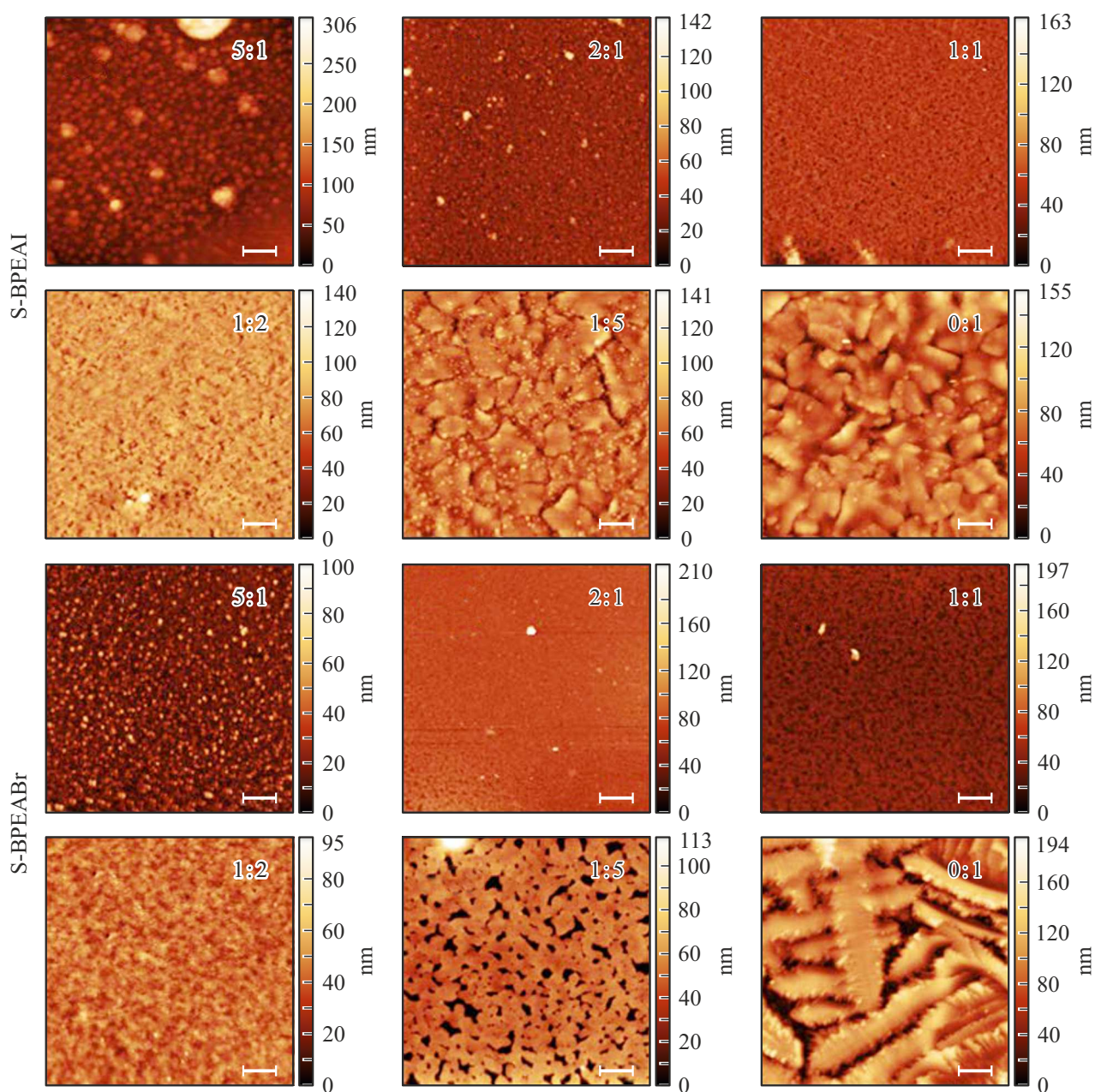


Figure 3. AFM images of the surface of quasi-2D perovskites obtained at various ratios of achiral and chiral precursors of MAI/S-BPEAX. Label size 2 μm .

When BPEAI is used, the position of the absorption bands and CD do not vary significantly, and if the BPEABr salt is added, a serial blue shift of this absorption band is observed from 493 nm to 475 nm, which is related to the appearance and gradual increase in the quantity of bromine ions in the anionic substructure of perovskite, causing the increase in the width of the material band gap [19]. In this range the factors of absorption dissymmetry increase with the increased content of chiral salt added in synthesis (Table 2). Besides, the additional introduction of bromine ions increases the factor of absorption dissymmetry ($2.2 \cdot 10^{-4}$ for BPEAI compared to $3.3 \cdot 10^{-4}$ for BPEABr,

which is comparable to the data presented in the literature for the similar materials [20]). It is also worth noting that if S-BPEABr salt is used, the sign of the factor of dissymmetry changes with the change of the ratio of chiral and achiral cations. For the ratio of 5:1 the sign is negative, which indicates higher sensitivity to *R*-polarization, for concentrations of 2:1 and 1:1 it stays around zero, and at 1:2 and above it becomes positive. Similar change in the sign of the dissymmetry factor depending on the concentration of the chiral cation was already noted for two-dimensional perovskites and may be related to the change of the crystallization process in virtue of different

mutual orientation of chiral molecules depending on their concentration [21].

To use the film of the chiral quasi-two-dimensional perovskite as the active layer of the CPR photodetector, a high degree of its surface evenness is required [22]. As you can see from AFM images shown in Fig. 3, and also from Table 2, the morphological characteristics of the studied samples strongly depend on the MAI/S-BPEAX ratio. The significant imbalance of the molar ratio both towards MAI or S-BPEAX causes deterioration of the surface morphology. Most even films are obtained at the precursor ratio of 2:1, and the corresponding values of surface roughness make 6 ± 2 nm for S-BPEABr and 8 ± 2 nm for S-BPEAI. As the quantity of the chiral salt increases, first a fine-grained structure appears, and then large crystallites (up to $2 \mu\text{m}$) for S-BPEAI emerge, or a coarse-grained structure with pronounced combs and significant height differences is formed for S-BPEABr, which indicates a radical change in the crystallization mechanism at high concentrations of chiral salts. Probably, these structural changes happening upon introduction of excessive quantity of chiral cation, and cause qualitative changes in the spectra of circular dichroism shown in Fig. 2, *d*. For the formation of the devices on the basis of this material, the optimal variant is using the ratio of 2:1 with S-BPEAI, which achieves minimum roughness (8 ± 2 nm), and there is also a chiroptic response, which is reflected in the value of the factor of absorption dissymmetry $0.85 \cdot 10^{-4}$. It should also be noted that all samples of chiral quasi-2D-perovskites nevertheless have lower roughness compared to the reference sample produced without the addition of the chiral cation.

Conclusion

This paper presents the synthesis and characterization of quasi-two-dimensional perovskites with different ratios of achiral cation MAI and chiral cation S-BPEAI or S-BPEABr. Perovskites created using S-BPEAI/Br have the signal of circular dichroism of absorption in two ranges of wavelengths 480–500 and 300–450 nm. The presence of the additional bromine atom in the structure of the S-BPEA molecule (compared to the reference S-MBA) causes the increase in the film photoconductivity by an order of magnitude, besides, the factors of absorption dissymmetry maintain the value comparable to the literature data for such materials. The dissymmetry factor values in the band 480–500 nm at minimum roughness of the film surface are $2.2 \cdot 10^{-4}$ for MAI/S-BPEAI and $3.3 \cdot 10^{-4}$ for MAI/S-BPEABr. Subsequent increase in the content of the chiral cation causes increase in the factor of absorption dissymmetry, but is accompanied with the deterioration of the film surface morphology.

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Conflict of interest

The authors declare no conflict of interest.

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