Optical anisotropy is essential for the polarization-sensitive optoelectronic devices. Recently, in-plane anisotropic physical properties were demonstrated in several 2D layered materials such as black phosphorus (BP) [3, 4], GaTe [5], ReSe2 [6], SnS [7] and SeGe [8] due to their low-symmetry crystal structures. Especially, anisotropic light–matter interaction such as absorption, photoluminescence (PL), Raman and photocconductivity have been extensively studied in these low-symmetry layered materials [9]. Optical anisotropy not only facilitates the fundamental investigations of light–matter interaction, but also enables applications in polarization-sensitive photodetectors, polarization controller, polarization-resolved imaging, linear polarization light source and so on [2, 10]. For practical applications, it is desired to have materials with excellent optical properties and high anisotropy simultaneously.

In recent years, organic–inorganic hybrid perovskites have received considerable attention for their excellent optical and optoelectronic properties such as high quantum yield, tunable bandgap, large exciton binding energy, long diffusion length and so on [11–13]. It has been demonstrated that organic–inorganic hybrid perovskites have promising applications in solar cells, light emitting diodes, photodetectors and nano lasers [14–17]. Though organic–inorganic hybrid perovskites possess excellent optical properties, their optical anisotropy is rarely studied. Recently, our group reported a polarization sensitive photodetector based on 2D perovskite (iso-BA)2PbI4 thanks to the in-plane anisotropy, which indicates that organic–inorganic hybrid perovskites can provide the merit of excellent optical properties and anisotropy simultaneously [18]. Compared
with 2D configuration, 1D perovskites have unique chain crystal structure and are believed to provide a much higher anisotropy [19]. In addition, lower dimensionality system has lower deformation energy and thus lead to stronger electron-phonon interaction, which makes it easier to generate self-trapped excitons [20]. In the case of 1D perovskites, PL spectrum is dominated by the self-trapped excitons with broadband white-light emission and large Stokes shift [21–23]. Overall, 1D perovskites hold great potentials in the application of broadband polarization sensitive optoelectronic devices.

Herein, we have successfully synthesized bulk crystalline 1D organic lead iodine perovskites $\text{C}_4\text{N}_2\text{H}_14\text{PbI}_4$ with edge sharing octahedral lead iodine chains. PL spectrum of the 1D perovskite crystals is dominated by the broadband self-trapped exciton emission. We then investigate the emission, excitation and reflection anisotropy of the 1D $\text{C}_4\text{N}_2\text{H}_14\text{PbI}_4$ crystal systematically. An emission linear dichroic ratio of 5.5 and an excitation linear dichroic ratio of 7 have been achieved. In addition, we also find that the linear dichroic ratio is highly dependent on the temperature.

**Results and discussion**

1D perovskite $\text{C}_4\text{N}_2\text{H}_14\text{PbI}_4$ single crystals were synthesized by an aqueous solution method based on previous report [24] (see methods). The 1D structure is shown in figure 1(a), where the edge sharing octahedral lead iodine chains $\text{PbI}_4^{2-}$ are surrounded by the organic cations $\text{C}_4\text{N}_2\text{H}_14^+$. The structure can be considered as the bulk assembly of a 1D core–shell quantum wire. The as-synthesized $\text{C}_4\text{N}_2\text{H}_14\text{PbI}_4$ crystals exhibit yellow color and a size around half millimeter as shown in figure 1(b). The scanning electron microscopy image of crystals indicates smooth faces as displayed in figure 1(c). The x-ray diffraction (XRD) pattern of the crystals presents three strong sharp diffraction peaks as shown in figure 1(d), which can be indexed to monoclinic structure and confirms the formation of 1D perovskite crystals according to the previous report [25]. The narrow peaks also reflect excellent crystalline quality of our as-grown samples.

We first investigated the optical properties of the bulk 1D $\text{C}_4\text{N}_2\text{H}_14\text{PbI}_4$ crystals. Figure 2(a) shows the absorption (blue) and PL (black) spectra of the bulk crystals at room temperature. The observed two absorption
peaks at 425 nm and 520 nm are assigned to free exciton emission and self-trapped exciton emission respectively, which is consistent with previous report that free excitons and self-trapped excitons coexist under the equilibrium of thermal activation at room temperature [26]. The PL spectrum exhibit a high energy narrow band of free exciton emission at 455 nm and a low energy broad band self-trapped exciton emission at 600 nm respectively. It can be observed that the Stokes-shifted broad self-trapped exciton emission covers the whole visible range with a full width at half maximum of 147 nm at room temperature. Figure 2(b) displays the temperature dependent PL of 1D C4N2H14PbI4 crystals. The redshift of PL peak with decreasing temperature can be attributed to change of bandgap energy due to the thermal effect, electron-phonon interaction and electronic band structure variation similar to the previous report [27]. As the temperature decreases, the interaction between orbital of Pb and I in the valence band maximum state is enhanced due to thermal shrink of the lattice and therefore the energy gap becomes narrower [28–30]. The PL peak energy shift is around 89 meV when the temperature decreases from 296 to 80 K (figure S1 is available online at stacks.iop.org/JPHOTON/2/014008/mmedia) while the PL intensity of 1D C4N2H14PbI4 crystals increases dramatically with the decrease of temperature (figure S2). Shibata developed the multilevel radiative decay model to analyze the phenomenon [31]. In this model, the change of PL intensity with temperature is mainly caused by quenching effect [32]. The quenching effect is composed of several mechanisms: (1) thermal dissociation of the electron-hole pair [33], (2) with the temperature increasing, the excitons changing from the radiative self-trapped exciton states to the less radiative free exciton states [34], which leads to the decrease of the emission intensity with temperature increasing. Figure 2(c) shows the excitation power dependent PL spectra at 80 K. The extracted PL intensity versus excitation power is plotted in figure 2(d) and can be well fitted by a linear function. The linear dependence on the excitation power suggests the emission is indeed from the self-trapped excitons rather than the permanent defects [35]. If the emission is from the permanent defect, PL intensity will saturate when these traps are filled as reported in previous literature [35]. It is also noted the free exciton emission disappears at 80 K (figure 2(c)) while presents at room temperature (figure 2(a)), which is due to that all excitons are in self-trapped

Figure 2. Optical properties of 1D perovskite crystals. (a) Absorption (blue line) and emission (black line, excited at 405 nm) spectra of the bulk 1D perovskite crystals at room temperature. (b) Temperature dependent PL spectra of 1D C4N2H14PbI4 perovskite crystals ranging from 80 to 296 K. (c) Excitation power dependent PL spectra of 1D C4N2H14PbI4 perovskite crystals. (d) PL intensity versus excitation power at 80 K.
states at low thermal activation (80 K) and lead to pure broadband self-trapped exciton luminescence. As the temperature decreases, the thermal fluctuations of lattice cannot provide enough energy to stimulate the self-trapped excitons to form free excitons [36]. Please be noted that the weak free exciton around 455 nm is hardly to see at 296 K in figure 2(b) due to the scale issue; however, it can be clearly observed in the zoom-in spectrum in figure 2(a).

We further investigated the emission anisotropy of the 1D C4N2H14PbI4 crystals. In order to eliminate the influence from absorption anisotropy, we utilized a circularly polarized light to excite the samples. A polarizer is used to selectively detect the polarization of emission. Figure 3(a) shows the typical emission spectra at three representative angles of 0, 90 and 300 degree, which indicates the presence of significant emission anisotropy. To fully explore the emission anisotropy, the emission intensity from 0 to 360 degree in a 30 degree step is fully measured and displayed in figure 3(b). The angle dependent emission is well fitted with a function of

$$I(\theta) = I_0 \cos(2\theta + \varphi) + I_1$$

where $\theta$ is the angle of polarization of emission light, $\varphi$ is the parameter for initial phase when the polarized emission light is at the angle of 0 degree, and $I_0$ and $I_1$ are the intensity for polarized emission light and the components which are independent of polarized light, respectively. A two-lobe shaped curve can be resolved, which is originated from the chain structure of the 1D perovskite crystals. To characterize the magnitude of the anisotropy, the linear dichroic ratio is introduced, which is defined as the ratio of the maximum and minimum emission intensity ($I_{\text{max}}/I_{\text{min}}$) when we change the detection polarization angle from 0 to 360 degree. The linear dichroic ratio depends on the temperature and is around 3 at 140 K (figure S2). Figure 3(c) shows the temperature dependent linear dichroic ratio and it can be found the ratio increases with temperature, which may be due to that the lattice has different thermal expansion coefficient at different axis. The linear dichroic ratio reaches 5.47 at 260 K, which is much larger than the in-plane anisotropy of 2D layered materials.

In addition to the emission anisotropy, we also studied excitation anisotropy. Figure 4(a) displays the 2D color map of the PL intensity at various excitation polarization and emission polarization angles at 140 K. It can be observed that the emission is anisotropic at fixed excitation polarization, which is consistent with the results in figure 3. Moreover, the PL intensity also depends on the excitation polarization at fixed emission angle. The linear dichroic ratio at different linear excitation polarization is extracted and plotted in figure 4(b). Similar to the emission anisotropy, the linear dichroic ratio also exhibits a two-lobe shape with the excitation polarization angle. The largest excitation linear dichroic ratio of 7 can be achieved as shown in figure 4(b). The anisotropic PL under different excitation is probably originated from the anisotropic absorption.

Furthermore, we also investigated the reflectivity anisotropy of the 1D C4N2H14PbI4 crystals. For the reflectivity measurement, the source is unpolarized white light and reflection signal is collected at different polarization angles. Figure 5(a) shows the reflectivity spectra at the typical angles of 0, 90 and 300 degree (140 K), which suggests that the reflectivity of 1D perovskite crystals also exhibits significant anisotropy. The reflectivity peaks at 445 and 610 nm are corresponding to the free and self-trapped excitons respectively, which is consistent with the absorption spectrum shown in figure 2(a). It is noted that the free exciton around 445 nm can be observed in reflection spectrum (figure 5(a)) but absent in the PL at 140 K (figure 2(b)), which is attributed to the different microscopic process in PL and reflection. For photoluminescence, the thermal fluctuations of lattice cannot provide enough energy to stimulate the self-trapped excitons to form free excitons at a low temperature. Consequently, only the recombination of self-trapped excitons can be observed at 140 K. In the case of reflection, it closely relates to both real and imaginary part of the dielectric constant via formula $R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}$.
where \( n \) represents the refractive index and \( k \) is the extinction coefficient of 1D perovskites. Since both \( n \) and \( k \) do not vanish at the energy of the free exciton, we anticipate that reflection should be present at 140 K [37].

The complete collection polarization angle dependent reflectivity of free exciton (445 nm) and self-trapped exciton (610 nm) are shown in figures 5(b) and (c), respectively. Similar to the excitation and emission anisotropy, the reflectivity also exhibits a two-lobed shape. The reflectivity linear dichroic ratio is around 1.3 at 140 K. We also measured the reflectivity anisotropy at different temperature (figure S3) and the extracted reflectivity linear dichroic ratio is plotted in figure 5(d). Both the reflectivity linear dichroic ratio of free exciton and self-trapped exciton decreases first and then increases with increasing temperature, which is different with

Figure 4. Anisotropy of excitation. (a) 2D color map of anisotropy at 140 K. The x-axis and y-axis denote the emission polarization angle and the excitation polarization angle, respectively. The anisotropy can be reflected by the change of color. The step of excitation polarization angle and emission polarization angle are both 30 degree. (b) Linear dichroic ratio at different excitation polarization at 140 K.

Figure 5. Anisotropy of reflection. (a) Reflection spectra at different collection polarization angles at 140 K. (b), (c) Polarization angle dependent reflectivity at 445 and 610 nm, respectively. The red curve is the fitting result. (d) Temperature dependent linear dichroic ratio of reflection at 445 and 610 nm.
the emission anisotropy. This is might be due to the fact that the reflection spectra reflect more on the absorption anisotropy. Nonetheless, more investigations are required to clarify this.

The large optical anisotropy can be traced to the transition dipole moment anisotropy and the quantum confinement effects [38, 39]. Firstly, 1D perovskite C₄N₂H₁₄PbI₄ crystals have the intrinsic dipole moment anisotropy due to the 1D chain structure. Secondly, the lattice distortion also can induce extrinsic dipole moment anisotropy [40]. The diameter of I⁻ is large enough to induce the lattice distortion. Furthermore, 1D organic lead iodine perovskite C₄N₂H₁₄PbI₄ crystals with edge sharing octahedral lead iodine chains [PbI₂⁺] sitting in the columnar cages created by the C₄N₂H₁₂⁺ cations. This unique 1D structure results in strong quantum confinement effect with the formation of self-trapped excited states, which causes the anisotropy of optical matrix element and thus the optical anisotropy. Because the interaction along the chain axis is much stronger than the perpendicular direction, we assume the temperature dependent anisotropy is mainly due to thermal expansion along the direction perpendicular to the chain axis [41, 42].

Conclusions

In conclusion, high quality 1D C₄N₂H₁₄PbI₄ crystals are synthesized by an aqueous solution method. The emission, excitation and reflectivity anisotropy of the as-synthesized 1D C₄N₂H₁₄PbI₄ crystals are investigated. The PL of 1D C₄N₂H₁₄PbI₄ crystal is dominated by the broadband self-trapped exciton emission and the emission linear dichroic ratio is up to 5.47 at 260 K. In addition, 1D C₄N₂H₁₄PbI₄ crystal also exhibits an excitation linear dichroic ratio of 7, which is much larger than the in-plane anisotropy of 2D layered materials. The origin of excitation anisotropy is attributed to the absorption anisotropy, which is confirmed by the reflectivity anisotropy. We interpret that the anisotropic dipole moment and quantum confinement of the 1D structure are responsible for the decent optical anisotropy. Our results not only advance the optical anisotropy of 1D perovskites, but also provide a new option for broadband polarization-sensitive optoelectronic devices within the whole visible range.

Methods

Materials

Lead iodine (PbI₂, 99.99%), hydroiodic acid (57 wt% in H₂O), and methylamine (CH₃NH₂, 40% in H₂O) were purchased from Sigma-Aldrich. N,N'-dimethylethylenediamine (C₄H₁₂N₂, 99%) was bought from DiBai Chemistry Company (Shanghai, China).

Synthesis of C₄N₂H₁₄PbI₄ bulk single crystals

Under a constant magnetic stirring, PbI₂ powder (0.05 g) was first mixed with 3 ml deionized water while 3 ml 57 wt% hydrogen iodine aqueous (HI) was added into the prepared PbI₂ solution, resulting in the rapid dissolution of the PbI₂ in the mixed solution with an increased pH value. The resultant solution was further stirred for about 5 min to obtain a clear solution. Finally, 2 ml mixture amine solution (CH₃NH₂:C₄H₁₂N₂ = 7:3, the ratio is volume of the solution) was slowly dropped into the clear solution. The stirring was then discontinued, and the solution was left to stand overnight. The 1D C₄N₂H₁₄PbI₄ crystals were obtained and collected by suction filtration and dried thoroughly.

Material characterizations

Optical microscope image and scanning electron microscope image were acquired by an Olympus BX53 system and a tungsten filament scanning electron microscope (TESCAN), respectively. The XRD pattern was collected in a Bruker D2 PHASER (Cu Kα λ = 0.15419 nm, Nickel filter, 25 kV, 40 mA).

Optical measurement

The schematic illustration of the optical measurement is displayed in figure S4. A 405 nm solid state laser was used as excitation source for PL and excitation anisotropy measurement. A 1/4 waveplate was used to generate circularly polarized light for PL anisotropy measurement while the polarization of emitted light was analyzed by a linear polarizer. The signal was collected by a home-built Raman spectrometer (iHR 550) equipped with a 600 lines/mm granting in a backscattering configuration. For the excitation anisotropy measurement, a half-waveplate was used to tune the polarization of the excitation laser. The measurement of reflectivity anisotropy is similar with PL measurement, except that a broad-spectrum light source was used as the light source and the background signal was measured by a silver mirror first. In terms of low-temperature measurement, a liquid
nitrogen continuous flow cryostat (Industry of America, USA) coupled with a temperature controller (Lake Shore Model 336) was used to provide the continuous temperature variation from 77 K to room temperature.

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