Direct detection of circular polarized light in helical 1D perovskite-based photodiode

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Detection of circularly polarized light (CPL) has a high potential for development of various optical technologies. Conventional photodetectors require optical polarizers on the device to detect polarized light, and this causes substantial losses of sensitivity and resolution in light detection. Here, we report direct CPL detection by a photodiode using a helical one-dimensional (1D) structure of lead halide perovskites composed of naphthylethylamine-based chiral organic cations. The 1D structure with face-sharing (PbI₄)⁻⁺ octahedral chains whose helicity is largely affected by chiral cations shows intense circular dichroism (CD) signals over 3000 mdeg at 395 nm with the highly anisotropic factor (g_CD) of 0.04. This high CD enables photocurrent detection with effective discrimination between left-handed and right-handed CPLs. The CPL detector based on this 1D perovskite achieved the highest polarization discrimination ratio of 25.4, which largely surpasses the direct detecting CPL devices (<4) using chiral plasmonic metamaterials and organic materials.

INTRODUCTION

In transaction of optical information, main functions of light source are intensity, color (wavelength), and polarization. Polarization of light can be used for object identification, contrast enhancement, navigation, and communication through polarization reflections (1–3). This function also has a high potential for application in various optical technologies and devices like security system (4), remote sensing (5), quantum signal detection (6), and substance screening (7). Although a few animal species like stomatopod crustaceans have developed a visual system capable of detecting and analyzing circularly polarized light (CPL) (8, 9), humans are normally unaware of any aspect of polarized light. In general, to detect polarized light refracted from a substance, linear polarizer and quarter-wave plate are attached on top of the conventional photodetectors using an inorganic semiconductor like Si and GaAs, which cannot detect polarized light directly. These device structures cause substantial losses of sensitivity and resolution in the light detection system.

CPL arises when the electric field rotates in a circle around the direction of propagation and it is called left- or right-handed CPL depending on the rotation direction. Circular dichroism (CD) is the differential absorption of left- and right-handed CPLs, which can be observed in absorption bands of any optically active molecule or secondary structure with chirality. Direct CPL detection has been reported by using such chiral materials. Yang et al. (10) demonstrated a CPL detecting organic field-effect transistor based on an asymmetrically pure, helically shaped chiral semiconductor molecule known as a helicene. Recently, Schulz et al. (11) used enantiopure semiconducting squaraine molecule derivatives of opposite handedness in bulk heterojunction photodiode for detection of CPL. These photodetectors, however, show lower responsivity (R, less than 10 mA W⁻¹) than the commercial inorganic photodiode with quite low polarization discrimination ratio, R_l/R_R, because of their intrinsically low CD signals (~100 mdeg), which make their practical applications for sensitive CPL detection difficult.

Lead halide perovskites have been synthesized by using chiral ligands like 1-phenylethylamine (1-PEA⁺), resulting in formation of a chiral structure as zero-dimensional (0D), 1D, 2D, quasi-2D, and 3D (12, 13). The first structural report for 1D and 2D chiral perovskites was presented as a single crystal by Billing et al. (14, 15) in 2013. Ahn et al. (16, 17) demonstrated the chiroptical property in 2D chiral perovskites, (R- or S-1-PEA)₂PbI₄, by measurements of CD signals. The chiral ligand, R- or S-1-PEA⁺, also forms 1D chiral perovskites as (R- or S-1-PEA)PbI₃, and the CPL photodetector based on 1D chiral perovskite was reported by Chen et al. (18). Although they successfully achieved a higher responsivity of 797 mA W⁻¹, there is a crucial issue due to low polarization discrimination ratio between left- and right-handed CPL detection [R_l/R_R = 1.1, which is calculated by the value reported as 2(R_l – R_R)/(R_l + R_R) = 0.1].

Here, we show the preparation of a helical 1D structure in lead halide perovskites for efficient detection of CPL signals as a direct CPL detector. One-dimensional structure is composed of face-sharing (PbI₄)⁻⁺ octahedral chains, in which the helicity of the chains is largely affected by chiral cations with aromatic structures. Here, we selected R- (+) and S- (−) 1- (1-naphthylethylamine (R- and S-NEA⁺); Fig. 1A) as a chiral cation in the 1D perovskite. The large π-conjugated naphthalene skeleton in NEA⁺ can interact with neighbor molecules in the crystal and strongly affect the helicity of (PbI₄)⁻⁺ octahedral chains. The helical 1D perovskites with NEA⁺ show the largest CD signals ever reported in chiral perovskites with 1D or 2D structures, and thus, the photodiode with the inorganic helical chain extending to the carrier transporting direction exhibits an extremely sensitive CPL detection with high polarization discrimination ratio.

RESULTS AND DISCUSSION

Dimension control of perovskite crystal films

The dimension, 1D or 2D, of perovskite films was controlled by the molar ratio of NEA⁺ to Pb⁺⁺ in the precursor solution [(R- or S-NEA):PbI₂ = 2:1, 1:1, 0.75:1, and 0.5:1]. Figure 1B shows x-ray diffraction (XRD) patterns of perovskite films prepared with (R- or S-NEA):PbI₂ = 2:1 and 0.75:1 in the precursor solution. The perovskite film with 2:1 composition showed sharp diffraction peaks at 5.83°, 11.7°, 12.7°, 16.3°, 17.6°, 23.5°, and 29.5°, which are assigned

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to (002), (004), (013), (113), (006), (008), and (0010), respectively. The unit cell parameters were determined as $a = 8.738$ Å, $b = 9.534$ Å, $c = 30.266$ Å, and $\alpha = \beta = \gamma = 90^\circ$. The crystal structure can be confirmed as a 2D perovskite (R-(or S)-NEA)$_2$PbI$_4$ with the $P2_12_12_1$ chiral space group by Rietveld refinements and the geometry optimization based on the density functional theory (DFT) calculation (Fig. 1C and fig. S1) (19). In 2D layers, the (PbI$_6$)$^{4-}$ octahedra share four corners of equatorial halides and form infinite sheets in the $ab$ plane. The chiral organic molecules, NEA$^+$, are located between the inorganic layers. Such a layer arrangement is similar to the structure already reported in chiral 2D perovskite using 1-PEA$^+$ (inorganic layers). Such a layer arrangement is similar to the structure of (NEA)$_2$PbI$_4$ (15). It indicates that the large $\pi$-conjugated naphthalene skeleton of NEA$^+$ strongly interact with neighbor molecules. The large intermolecular interaction of chiral organic molecules in 2D structure influences the distortion of (PbI$_6$)$^{4-}$ octahedral structure (fig. S1B), which will enhance the chirality on an achiral (PbI$_6$)$^{4-}$ part.

The perovskite films made from 0.75:1 and 0.5:1 composition form a completely different crystal structure from 2D. The diffraction peaks were observed at 6.84°, 10.2°, 11.3°, 13.2°, 13.7°, and 24.3°, corresponding to (002), (011), (102), (110), (004), and (013), respectively. The unit cell parameters were $a = 9.889$ Å, $b = 9.256$ Å, $c = 25.812$ Å, and $\alpha = \beta = \gamma = 90^\circ$. The results of Rietveld refinements for optimization of the crystal structure showed that the crystal film formed 1D structure as (NEA)PbI$_3$, where face-sharing (PbI$_6$)$^{4-}$ octahedral chains closely interacted with NEA$^+$ cations (Fig. 1D and fig. S2). (R (or S)-NEA)PbI$_3$ also has a chiral space group of $P2_12_12_1$. In (R(or S)-NEA)PbI$_3$, chiral NEA$^+$ cations surround the (PbI$_6$)$^{4-}$ chain and give a larger helicity to the chain by strong interaction between an achiral (PbI$_6$)$^{4-}$ and a chiral NEA$^+$ than that of 2D structure with the interaction between the plane and chiral molecules. The inter-chain spacing ($d/2$) was 12.9 Å, which corresponds to the distance between helical chains. The yield of the 1D structure was optimized with a low molar ratio of NEA$^+$ (0.5 to 0.75) with respect to PbI$_2$. When the film was prepared by the precursor solution of NEA$^+$ and PbI$_2$ with the stoichiometric ratio of 1:1, the mix structures of 1D and 2D were obtained (fig. S3). It means that the formation speed of 2D structure may be faster than that of 1D. That is, a stoichiometric ratio in solution is important to obtain a pure 1D film. In addition, in 1D film, the smooth surface was obtained by addition of methylammonium (MA) into the precursor solution (fig. S4), indicating that addition of MA slowed the crystal formation speed of 1D structures. The surface of the perovskite film largely affects the device performance as shown later. There was no observation of MAPbI$_3$ and PbI$_2$ crystal phase, generally observed at 14° and 12.7°, respectively (20).

To clarify the orientation of perovskite domains in low-dimensional structures, which affects charge carrier transport properties in the optoelectronic devices (21), we carried out 2D grazing-incidence wide-angle x-ray scattering (2D-GIWAXS) measurements. Figure 1 (E and F) shows 2D XRDs of 2D (R-(or S)-NEA)$_2$PbI$_4$ and 1D (R-(or S)-NEA)PbI$_3$ perovskite films, respectively. The strong diffraction peak was assigned to (002) plane, which arises from the distance between layers in 2D and between chains in 1D. In the 2D film, the strong diffraction spot appeared in out-of-plane direction. The $\chi$ rocking curve produced by the (002) diffraction profile along arc-like feature (Fig. 1E, inset) was found to be sharp with the full width at half-maximum of 6.5°. It indicates that layer structures of the 2D film are highly oriented in parallel to the substrate. On the other hand, the (002) reflection in the 1D structure spread along Debye-Scherrer ring became strong between out-of-plane and in-plane direction around $\chi = 30^\circ$ (Fig. 1F, inset), meaning that 1D chains lie against the substrate.
The orientated layer or chain structures composed of octahedral (PbI₆)⁴⁻ contributes to the photoconductivity in the detector as shown later.

The difference in the organic-inorganic interaction between 1D and 2D structures was also observed in Fourier transform infrared (FTIR) spectra (Fig. 2 and table S1). NEA⁺ has −NH₃⁺ amine hydroiodide group and showed a weak N-H stretch band of −NH₂ at 3170 cm⁻¹, which was strongly observed at the lower energy of 3120 and 3050 cm⁻¹ in 1D and 2D structure, respectively. It means that hydrogen ion of −NH₃⁺ group strongly interacts with iodide ion of (PbI₆)⁴⁻, especially in 1D structure. A stretch band of −NH₃⁺ of (NEA)I at 1993 cm⁻¹ is also shifted to the lower energy side as broad and weak bands in 1D or 2D. The results are supported by crystal structures where NEA⁺ more strongly interacts with (PbI₆)⁴⁻ chain in 1D structure than with the plane in 2D. A small amount of MAPbI₃ was observed as a weak shoulder band around 3190 cm⁻¹, which hardly influences on 1D or 2D structure from the results of XRD.

Chiroptical properties of 2D and 1D perovskites

To examine the CPL response of our 1D and 2D perovskites, we carried out CD measurements. Figure 3 shows absorption and CD spectra of 1D-structured (R- and S-NEA)PbI₃ and 2D-structured (R- and S-NEA)₂PbI₄ films. The CD signals of the chiral organic small molecules are essentially weak in solution (22). (R- and S-NEA)I also showed weak CD signals as 1 mdeg with an opposite response at 280 nm (fig. S5). The anisotropy factor (gCD factor) was calculated as the following equation (23)

\[
g_{CD} = \frac{\text{CD [ mdeg]}}{32980 \times \text{Absorbance}} = \frac{\Delta A}{\text{Absorbance}}
\]

where \( \Delta A \) is the difference in absorption of the left-handed (A_L) versus right-handed (A_R) CPL (\( \Delta A = A_L - A_R \)). The gCD factors of (R- and S-NEA)I were estimated less than \( 1.0 \times 10^{-4} \).

The absorption bands significantly changed in forming low-dimensional perovskite structures. Two-dimensional structure (R- or S-NEA)₂PbI₄ films showed the excitonic absorption peaks at 488 nm (Fig. 3A), in which the conduction band consists of Pb 6p orbital, and the valence band mostly consists of 1p states with a small amount of Pb 5s (24). The CD signals from (R- and S-NEA)₂PbI₄ films were oppositely observed at the corresponding position, while the racemic 2D perovskite (rac-NEA)₂PbI₄ showed no CD signals (fig. S6). The gCD factor of CD was estimated as ~0.003 (fig. S7), which is one order of magnitude larger than that generally obtained with chiral organic molecules. It indicates that the incorporation of chiral organic cations to lead iodide perovskite promotes the large optical chirality in perovskite 2D structure. The optical chirality of 2D perovskites is largely enhanced by NEA⁺ compared with 1-PEA⁺ whose gCD factor is less than \( 10^{-3} \). It may result from the distortion of (PbI₆)⁴⁻ octahedral structures enhanced by NEA⁺ with a large \( \pi \)-conjugated naphthalene skeleton as shown in fig. S1. In chiral 2D perovskites, the bisignate CD pattern were observed at the absorption band edge with two peaks at 488 and 504 nm. This phenomenon can be explained by the splitting of the energy state with the opposite spin state of electron perturbed by chirality (25). Although the larger CD signals could be obtained by formation of chiral 2D structure with NEA⁺ than that of ordinary chiral materials, it is not enough to detect CPL sensitively with high polarization discrimination ratio.

Note that the 1D structure with helical (PbI₆)⁴⁻ chains showed quite intense CD signals more than 3000 mdeg (Fig. 3B). One-dimensional structure (R- and S-NEA)PbI₃ showed absorption bands at 375 nm. Compared with the sharp 2D excitonic absorption bands, the spectra of 1D were relatively broader. It results from flat bands and large bandgap of the face-sharing octahedral structure in 1D perovskite (26). The CD signals in 1D depend on the molar ratio of NEA⁺ and PbI₂ in the precursor solution. The highest value of CD was achieved in the 1D structured film made from the 0.75:1 precursor solution of NEA⁺ and PbI₂ (Fig. 3B and figs. S8 and S9). The (R- and S-NEA)PbI₃ exhibited oppositely signed CD patterns at the peak position of 395 nm with the highest intensity of 3200 mdeg (Fig. 3B). To confirm the origin of these intense CD signals, we also measured the linearly polarized (LD) spectra (fig. S10). The results showed no apparent difference in optical absorption of parallel and perpendicular polarized light (optical density difference, \( \Delta OD \)), meaning that the orientation in the film is small enough to be ignored and the CD signals are mainly originated from helical 1D structure of perovskites. No CD signals were observed in the racemic 1D perovskite (rac-NEA)PbI₃ (fig. S11). The gCD factor of CD at 395 nm is ~0.04 (fig. S12), which is two times larger than that of (R- or S-1-PEA)PbI₃ (18). It indicates that larger aromatic naphthyl parts induce larger helicity in 1D (PbI₆)⁴⁻ chains than phenyl parts induced chain structures. As a result, (R- and S-NEA)PbI₃ showed the highest gCD value in the chiral low-dimensional perovskites. The broad background around 500 nm
in absorption spectra comes from MAPbI$_3$, which coexists with 1D perovskite in the film. Although the absorption band of MAPbI$_3$ has no CD signals, the existence of MAPbI$_3$ accelerated the CD intensity of 1D structure. Only one-tenth of CD signals is observed in the 1D structure without MAPbI$_3$ (fig. S13), which only forms an amorphous-like film (fig. S14). It means that the crystallinity and the surface morphology of the 1D structured film are modified by the coexistence of MAPbI$_3$ and strongly affect the chiroptical property.

Figure 4 represents that the dimension of lead halide perovskites highly influences the chiroptical properties, which can be controlled by the concentration ratio of Pb$^{2+}$ to NEA$^+$. One-dimensional structure has an extremely larger chiroptical property than the 2D structure although the absorption wavelength shifts to the lower region.

**Direct detection of CPL signals in the helical 1D perovskite-based photodiod**

The high CD directly leads to effective discrimination in detection between left-handed circularly polarized (LCP) and right-handed circularly polarized (RCP) lights for application to photodetectors. We prepared a CPL photodetector with a bilayer structure comprising the helical 1D perovskite (R- and S-NEA)PbI$_3$ as a CPL absorber (Fig. 5A). The device structure is as follows: transparent conducting oxide (TCO)/SnO$_2$ (10 nm)/(R- and S-NEA)PbI$_3$ (220 nm)/bathocuproine (BCP) (15 nm)/Ag (80 nm) (see the Materials and Methods for details of device fabrications). An SnO$_2$ layer was coated on TCO glass by spin coating of SnO$_2$ nanoparticle suspended solution, which works as the electron-transport/hole-blocking layer. A BCP molecular layer as hole-transport/electron-blocking layer was deposited on the 1D perovskite layer by thermal evaporation under vacuum. Figure 5B shows the photocurrent density–voltage (J-V) characteristics of the (R-NEA)PbI$_3$ device under LCP and RCP light at the wavelength of 395 nm with an intensity of 1 mW cm$^{-2}$. Under unpolarized light, the device exhibited photocurrent with a density over 10$^{-4}$ A cm$^{-2}$ under reverse bias voltage (0 to −1 V, fig. S15), while the dark current was suppressed well to 10$^{-6}$ A cm$^{-2}$. Such a low dark current dominates the noise current of the photodetector, which was achieved in the 1D film with the smooth surface obtained by addition of MA into the precursor solution (fig. S4), which are supported by the observation of large leak current in the 1D film without MA.

Photocurrent outputs on the incidence of LCP light show similar behavior with signals over 10$^{-4}$ A cm$^{-2}$, while that under RCP light with the same light intensity was less than 10$^{-5}$ A cm$^{-2}$. The difference of photocurrent intensity corresponds to the opposite sign of CD response as shown in Fig. 3B. The same behavior was observed in the device using (S-NEA)PbI$_3$, where large photocurrent over 10$^{-4}$ A cm$^{-2}$ was observed under RCP light irradiation (fig. S16).

The external quantum conversion efficiency (EQE; incident photon-to-current conversion efficiency) was calculated as Eq. 3

$$\text{EQE (\%) = } \frac{J_{\text{ph}} \cdot \hbar c}{I_{\text{in}} e \lambda} \times 100 = \left(\frac{J_{\text{light}} - J_{\text{dark}}}{I_{\text{in}}} \cdot \frac{\hbar c}{e \lambda}\right) \times 100 \quad (3)$$

where $J_{\text{ph}}$ is photocurrent density, $J_{\text{light}}$ is current density under CPL irradiation, $J_{\text{dark}}$ is background dark current density, and $I_{\text{in}}$ is the incident light intensity. $\lambda$, $e$, $h$, and $c$ are the incident wavelength, electron charge, Planck’s constant, and speed of light, respectively. The (R-NEA)PbI$_3$ device yielded a photocurrent signal of 2.8 × 10$^{-4}$ A cm$^{-2}$ for incident LCP light of 395 nm with 1.0 mW cm$^{-2}$ at an applied voltage of −0.5 V (Fig. 5C). This output corresponds to a high EQE value of 87.5%. On the other hand, the photocurrent output with RCP light was 1.2 × 10$^{-5}$ A cm$^{-2}$ with a low EQE of 3.4%. The corresponding responsivity (R) calculated as the ratio of the photocurrent and the incident light intensity ($I_{\text{in}}$) in (R-NEA)PbI$_3$ under LCP and RCP light irradiation (1.0 mW/cm$^2$) are 0.28 and 0.011 A W$^{-1}$, respectively. The polarization discrimination ratio $R_L/R_R$ of our helical 1D CPL detector was obtained as an extremely high value of 25.4, which largely surpasses those of the field-effect transistor–type chiral photodetector using chiral plasmonic metamaterials and organic materials ($R_L/R_R < 4$) (10, 27).

Note that the $R_L/R_R$ value of the 2D perovskites on CPL detection was as low as 1.2 (fig. S17 and table S2). It may be due to intrinsically low photocurrent response in 2D structure in which (PbI$_3$)$_x$-carrier-transporting planes are stacked perpendicular to the bilayer electrode. In contrast, the 1D chain extends to the carrier transporting direction in the device, resulting in the higher photocconductivity than 2D structure. In addition, the high photocconductivity in the helical 1D structure under CPL irradiation probably depends on the direction of the polarized electronic spin generated by selective absorption of CPL with angular momentum (17, 28). These effects have been reported in chiral perovskites with strong spin–orbit coupling, which can be explained by spin-dependent optical selection rules and large Rashba splitting (29–31). As these results, our CPL detector with helical 1D perovskites successfully generated the unexpected highly polarization exciton ratio.

In conclusion, we have demonstrated the large chiroptical properties enabled by a helical 1D structure in lead halide perovskites using NEA$^+$ as a chiral organic cation. The dimension was controlled from 2D to 1D by the concentration ratio of Pb$^{2+}$ to NEA$^+$ in the precursor solution. The 2D and 1D crystal structures were confirmed by Rietveld refinements from powder diffraction data and the geometry optimization based on the DFT calculation, which have the $P_{2_1}2_12_1$ chiral space group. In the 1D structure, chiral NEA$^+$ cations surround the (PbI$_6$)$_x$ chain and give a larger helicity to the chain by strong interaction between an achiral (PbI$_6$)$_x$ and a chiral NEA$^+$ than that of 2D structure with interaction between the plane and chiral molecules. The helical 1D structure showed quite intense CD signals over 3000 mdeg with the highest g value of 0.04 in the chiral low dimensional perovskites, which results from a large helicity in

![Fig. 4. Relationship between the dimension of perovskites and chiroptical properties.](image)

The value of gCD factor (red line) and absorption wavelength (black line) with respect to concentration ratio of Pb$^{2+}$ to NEA$^+$ in the precursor solution.
1D (PbI$_6$)$_4$$^-$ chains induced by aromatic naphthyl parts in NEA$^+$. The CPL detector consisting of helical 1D perovskites as an absorber was fabricated, where the inorganic helical chain extends to extending the carrier transporting direction. The device generated the highest polarization discrimination ratio of 25.4 in the direct photocurrent-mode detection of CPL. The material and method of the chiroptical perovskites reported here would open its applications for a previously unidentified organic-inorganic semiconductor with potentials in a full stokes imaging for advanced optical devices.

**MATERIALS AND METHODS**

**Synthesis of (R- and S-NEA)I**

1-(1-naphthyl)ethylamine hydroiodide, (R- or S-NEA)I, was prepared by slowly mixing 1 g of R- or S-NEA (>99.0%, Tokyo Chemical Industry, TCI) with 0.5 ml of hydroiodic acid (55 weight %, FUJIFILM Wako chemicals) at 70°C for 1 hour. Here, 2D and 1D structures were obtained using 2.0 M and 0.5 to 0.75 M of (R- or S-NEA)I that give (NEA)I/PbI$_2$ ratios of 2 and <1, respectively. A small amount (0.05 to 0.1 M) of methylammonium iodide (>99.0%, TCI) is also added into the precursor to control the formation speed of the film. The precursor solution was spin-coated onto a glass substrate (quartz for optical measurements and TCO glass) at 100°C for 30 min. The obtained film thickness is 280 nm for 2D and 220 nm for 1D.

**Perovskite film preparation**

The chiral structures of lead iodide perovskite film with NEA$^+$ as cation were fabricated by one-step solution process. One molar PbI$_2$ (99.99%, TCI) and 0.5 to 2.0 M (R- or S-NEA)I were dissolved in dimethylformamide anhydrous solution (N,N$'$-dimethylformamide, 99.5+%, FUJIFILM Wako chemicals) at 70°C for 1 hour. Here, 2D and 1D structures were obtained using 2.0 M and 0.5 to 0.75 M of (R- or S-NEA)I that give (NEA)I/PbI$_2$ ratios of 2 and <1, respectively. A small amount (0.05 to 0.1 M) of methylammonium iodide (>99.0%, TCI) is also added into the precursor to control the formation speed of the film. The precursor solution was spin-coated onto a glass substrate (quartz for optical measurements and TCO for photodetectors) at 1000 rpm for 10 s and 5000 rpm for 60 s. Chlorobenzene (99.8%, Sigma-Aldrich) as an antisolvent was dripped by putting them under sonication for 10 min in each of the solvents and then dried by blowing N$_2$ gas. An SnO$_2$ blocking layer was coated on TCO glass by spin-coating a diluted aqueous solution of SnO$_2$ nanoparticle (15% in H$_2$O colloidal dispersion, Alfa Aesar, was diluted to be ~2% before being used) with 30 min of drying at 150°C. The perovskite films were deposited under ambient atmosphere as described in the perovskite film preparation section. On top of the perovskite films, BCP (purified by sublimation, >99.0%, TCI) was deposited by thermal evaporation under vacuum at pressures of below 5 × 10$^{-5}$ Pa. Then, Ag layer was lastly deposited on the top as counter electrode by vacuum evaporation. The active area of the device was 3 mm by 3 mm.

**Device fabrication**

TCO (an indium tin oxide–antimony-doped tin oxide composite) glass (15 ohm sq. −1, Geomatic Co. Ltd.) was cleaned sequentially with acetone, isopropanol, and deionized water by putting them under sonication for 10 min in each of the solvents and then dried by blowing N$_2$ gas. The TCO glass was lastly treated under ozone plasma for 10 min. An SnO$_2$ blocking layer was coated on TCO glass by spin-coating a diluted aqueous solution of SnO$_2$ nanoparticle (15% in H$_2$O colloidal dispersion, Alfa Aesar, was diluted to be ~2% before being used) with 30 min of drying at 150°C. The perovskite films were deposited under ambient atmosphere as described in the perovskite film preparation section. On top of the perovskite films, BCP (purified by sublimation, >99.0%, TCI) was deposited by thermal evaporation under vacuum pressures of below 5 × 10$^{-5}$ Pa. Then, Ag layer was lastly deposited on the top as counter electrode by vacuum evaporation. The active area of the device was 3 mm by 3 mm.

**Characterizations**

XRD patterns were measured by D8 DISCOVER (Bruker AXS K.K.) with Cu Kα radiation under the operation condition of 40 kV and 40 mA to determine the crystal structure of perovskite. The molecular alignment was carefully measured with 2D-GIWAXS coupled with a 2D detector. The crystal models including the cell parameters and the atomic positions were determined by using the MS Reflex Plus module within BIOVIA Materials Studio 2020 software package. The Rietveld method was used for refining crystal structure from powder diffraction data. The DFT calculation using DMol3 and Gaussian modules were also performed for the geometry optimization. The FTIR spectra were measured in attenuated total reflection (ATR) mode with a diamond crystal (ATR PRO ONE) using the FTIR/4600 (JASCO Corporation). CD spectra were recorded on a J-1500 spectrometer (JASCO Corporation). Absorption and LD spectra were also measured on the same equipment. The current density–voltage (J–V) and current density– time (J–T) characteristics were recorded by a digital source meter (Keithley 2450). The monochromatic light source of irradiation was a Max 350 Xe lamp (Asahi spectra) equipped with an ultraviolet-visible mirror module and CMS-100 single monochromator. The CPL was obtained using a linear polarizer and quarter-wave plate (Thorlabs). The light intensity was measured and calibrated by a Si photodetector connected with a power meter (Ophir Japan Ltd.).
REFERENCES AND NOTES

5. L. Nagdimunov, L. Kolokolova, D. Mackowski, Characterization and remote sensing of biological particles using circular polarization. J. Quant. Spectrosc. Radiat. Transfer 131, 59–65 (2013).

6. L. Cen, Z. Zhang, J. Zhang, S. Li, Y. Sun, Y. Zhao, F. Wang. State preparation and detector effects in quantum measurements of rotation with circular-polarization-entangled photons and photon counting. Phys. Rev. A 96, 053846 (2017).

7. B. Kunnen, C. Macdonald, A. Dorojin, S. Jacques, M. Eccles, I. Meglinski, Application of circularly polarized light for non-invasive diagnosis of cancerous tissues and turbid tissue-like scattering media. J. Biophotonics 8, 317–323 (2015).

8. T.-H. Chiou, S. Kleiologel, T. Cronin, R. Caldwell, B. Loeffler, A. Siddiqui, A. Goldizen, J. Marshall, Circular polarization vision in a stomatopod crustacean. Curr. Biol. 18, 429–434 (2008).

9. R. M. Templin, M. J. How, N. W. Roberts, T.-H. Chiou, J. Marshall, Circularly polarized light detection in stomatopod crustaceans: a comparison of photoreceptors and possible function in six species. J. Exp. Biol. 220, 3222–3230 (2017).

10. Y. Yang, R. C. da Costa, M. J. Fuchter, A. J. Campbell, Circularly polarized light detection by a chiral organic semiconductor transistor. Nat. Photonics 7, 634–643 (2013).

11. M. Schulz, F. Balzer, D. Scheunemann, O. Arteaga, A. Lützen, S. C. J. Meskers, M. Schiek, Chiral excitonic organic photodiodes for direct detection of circular polarized light. Adv. Funct. Mater. 29, 1900684 (2019).

12. G. Long, R. Sabatini, M. I. Saidaminov, G. Lakhwani, A. Rasmita, X. Liu, E. H. Sargent, W. Gao, Chiral-perovskite optoelectronics. Nat. Rev. Mater. 5, 423–439 (2020).

13. L. Wang, Y. Xue, M. Cui, Y. Huang. H. Xu, C. Qin, J. Yang, H. Dai, M. Yuan, A chiral reduced-dimension perovskite for an efficient flexible circularly polarized light photodetector. Angew. Chem. Int. Ed. Engl. 59, 6442–6450 (2020).

14. D. G. Billing, A. Lemmerer, Bis[(S)-2-phenethylammonium] tribromoplumbatate(I). Acta Crystallogr. E59, m381–m383 (2003).

15. D. G. Billing, A. Lemmerer, Synthesis and crystal structures of inorganic–organic hybrids incorporating an aromatic amine with a chiral functional group. CrystEngComm 8, 686–695 (2006).

16. J. AHN, E. Lee, J. Tan, W. Yang, B. Kim, J. Moon, A new class of chiral semiconductors: chiral-organic-molecule-incorporating organic–inorganic hybrid perovskites. Mater. Horiz. 4, 851–856 (2017).

17. J. AHN, S. MA, J.-Y. Kim, K. Kym, W. Yang, J. A. Lim, N. A. Kotov, J. Moon, Chiral 2D organic inorganic hybrid perovskite with circular dichroism tunable over wide wavelength range. J. Am. Chem. Soc. 142, 4206–4212 (2020).

18. C. Chen, L. Gao, W. Gao, C. Ge, X. DU, Z. Li, Y. Yang, G. Niu, J. Tang, Circularly polarized light detection using chiral hybrid perovskite. Nat. Commun. 10, 1927 (2019).

19. B. Delley, From molecules to solids with the DMol3 approach. J. Chem. Phys. 113, 7756–7764 (2000).

20. A. Ishii, A. K. Jena, T. Miyasaka, Photomultiplying visible light detection by halide perovskite nanoparticles hybridized with an organo Eu complex. J. Phys. Chem. Lett. 10, 5935–5942 (2019).

21. A. Ishii, A. K. Jena, T. Miyasaka, Fully crystalline perovskite-perylene hybrid photovoltaic cell capable of 1.2 V output with a minimized voltage loss. APL. Mater. 2, 091102 (2014).

22. H. Tanaka, Y. Inoue, T. Mori, Circularly polarized luminescence and circular dichroisms in small organic molecules: Correlation between excitation and emission dissymmetry factors. ChemPhotoChem 2, 386–402 (2018).

23. B. Nordén, A. Rodger, T. Dafforn, Chapter 2, in Linear Dichroism and Circular Dichroism: A Textbook on Polarized-Light Spectroscopy (Royal Society of Chemistry, 2010).

24. Y. Tang, X. Cao, Q. Chi, Two-dimensional halide perovskites for emerging new-generation photodetectors. J. Phys. Chem. C 121, 26655–26666 (2017).

25. N. Berova, L. Di Bari, G. Pescitelli, Application of electronic circular dichroism in configurational and conformational analysis of organic compounds. Chem. Soc. Rev. 36, 914–931 (2007).

26. L. Mao, P. Guo, M. Kepenekian, I. Hadar, C. Katan, J. Even, R. D. Schaller, C. C. Stoumpos, M. G. Kanatzidis, Structural diversity in white-light-emitting hybrid lead bromide perovskites. J. Am. Chem. Soc. 140, 13078–13088 (2018).

27. W. Li, J. Z. Coppins, L. V. Bestiero, W. Wang, A. O. Govorov, J. Valentine, Circularly polarized light detection with hot electrons in chiral plasmonic metamaterials. Nat. Commun. 6, 8379 (2015).

28. Z. Wang, M. Gao, X. Hao, W. Qin, Helical-chiroptical nanowires generated orbital angular momentum for the detection of circularly polarized light. Appl. Phys. Lett. 116, 053301 (2020).

29. P. Odenthal, W. Talmadge, N. Gundlach, R. Wang, C. Zhang, D. Sun, Z.-G. Yu, Z. Valy Vardeny, Y. S. Li, Spin-polarized exciton quantum beating in hybrid organic–inorganic perovskites. Nat. Phys. 13, 894–899 (2017).

30. G. Long, C. Jiang, R. Sabatini, Z. Yang, M. Wei, L. N. Quan, Q. Liang, A. Rasmita, M. Askerka, G. Walters, K. Gong, J. Xing, W. Ren, R. Quintero-Bermudez, H. Yuan, G. Xing, X. Renshaw Wang, D. Song, O. Voznyy, M. Zhang, S. Hoogland, W. Gao, Q. Xiong, E. H. Sargent, Spin control in reduced-dimensional chiral perovskites. Nat. Photon. 12, 528–533 (2018).

31. G. Long, Y. Zhou, M. Zhang, R. Sabatini, A. Rasmita, L. Huang, G. Lakhwani, W. Gao, Theoretical prediction of chiral 3D hybrid organic–inorganic perovskites. Adv. Mater. 31, e1807628 (2019).

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