Observation of unusual optical band structure of CH$_3$NH$_3$PbI$_3$ perovskite single crystal

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ABSTRACT

Extensive efforts have been undertaken on the photoelectric physics of hybrid organolead halide perovskites to unveil the reason for the attractive photovoltaic performance. Yet, the resulting evidence is far from being fully conclusive. Herein, we provide another direct support for this issue. In addition to the observation on the conventional band edge at 1.58 eV that presents a blueshift toward temperature increase, interestingly, we also observe an unusual optical band edge at 1.48 eV in CH$_3$NH$_3$PbI$_3$ perovskite single crystals for the first time. Contrary to the conventional band edge, this one shows an obvious redshift toward the enhancement in temperature, in agreement with the Varshni relation. More interestingly, the unusual band edge exhibits a series of obvious absorption and photocurrent signals, but the according photoluminescence signals are not observable. This indicates that this band edge is particularly beneficial for the photovoltaic effect due to the inhibited radiative recombination. The kinetics on photo-involved charge transition and transfer are investigated using the pump-probe photoconductivity technique, and a changeable band structure model was proposed.

KEYWORDS: optical band edge, CH$_3$NH$_3$PbI$_3$ perovskite, absorption signal, photoluminescence, pump-probe technique.
Hybrid organolead halide perovskites, MAPbX$_3$ (MA=CH$_3$NH$_3^+$, X = Cl, Br, I), have recently received worldwide attention as highly promising materials in solar cells, light-emitting diodes, photodetectors and lasers, attributing to the impressive characteristics including high absorption coefficient, long carrier lifetime and high balanced charge mobility.$^{1, 2, 3, 4}$ In particular, the efficiency of solar cells based on hybrid halide perovskites has been realized over 20% certified. Significantly, these devices are usually fabricated on the basis of a solution-processed procedure and the resulting perovskite films are generally polycrystalline.$^5, 6, 7$ This gives rise to a fundamental question: why such materials are so special in comparison with traditional semiconductors?

To address this issue, extensive efforts have been made for thoroughly elucidating the fundamental photophysics in MAPbI$_3$. Two main controversies, however, are still not well addressed yet. First, what is the real optical band gap ($E_g$) value of MAPbI$_3$ single crystal (MSC)? Some researchers reported that the $E_g$ of MSC was 1.51 eV (concluded from photoluminescence spectroscopy, PL)$^{8, 9}$ and 1.48 eV (from diffuse reflectance spectroscopy, DR).$^{10}$ However, more reported PL peak positions of MSC are located at 1.61 eV.$^{11, 12}$ This indicates that unlike in conventional semiconductors even the $E_g$, the most important parameter of a semiconductor, is not yet definitely determined in MSC. Second, the conventional consensus that MAPbI$_3$ behaves as a direct band gap semiconductor$^{13, 14}$ has to be modified, since recent theoretical calculations suggest that the relevant conduction band minimum is slightly shifted in k-space with respect to the valence band maximum, leading to an indirect fundamental band gap.$^{15, 16, 17}$ Then Hutter et al. have proposed that the band gap in MAPbI$_3$ has a direct-indirect character.$^{18}$ These controversies lead to another key question: what does the real band
structure of MAPbI$_3$ look like? This is of great significance to the dynamics of both generation and recombination of photo-generated charge carriers, which are far from being well clarified.

The combination of different optical techniques is more effective for a thorough understanding of optical and electronic properties of MAPbI$_3$ perovskite. Yamada, Kanemitsu et al. have determined the band gap energy of MAPbI$_3$ using PL, PC, DR, and other techniques in 2014. $^{13}$ This work is of significance to understand the energy band structures of perovskite. Herein, we use a modified PC-R system, the schematic of our PC-R system setup, is shown in Figure S1. Through this system, we could realize the in situ optical measurements for both photoconductivity (PC) and reflectance (R) spectra at the same time. This guarantees the accuracy of the results and enables us to observe the unusual optical band structure that have never been reported. We focus on the previously mentioned controversies and investigate the band structure of MSC using techniques based on temperature-dependent PC-R and PL spectroscopies, and pump-probe technique. Surprisingly, we observe an unusual band edge in MSC, which appears obviously in PC and R spectra while not in the relevant PL spectra. This indicates a high conversion efficiency of photon to electric. Details on the origin of this band structure is discussed herein.

■ EXPERIMENTAL METHODS

**Synthesis and characterization of MSCs.** MSCs as large as $6 \times 5 \times 3$ mm$^3$ were grown by a solution crystallization process. Equimolar mixture of the CH$_3$NH$_3$I and PbI$_2$ were dissolved in GBA (1, 4-Butyrolactone) for MAPbI$_3$. The concentration of MAPbI$_3$ was 1.2 M. The solution was stirred under 60 °C until it turned transparent. Then the
temperature increased with the speed of 5 °C per 30 min. We maintained the current temperature for 12 h till little black crystals were separated out. As the seed was put into fresh solution, heated and kept at the same temperature for one day, the original seed grew into a larger one. Using the larger crystal as the new seed and repeating the above process, a much larger crystal was obtained. The size of crystal increases in proportion to the repeating times. Then, the MSC was thinned and polished along one direction to 1.5 mm thickness using a mechanical method, in order to control the temperature of the crystal surface faster and more accurately. Finally, a pair of Au electrodes (100 nm of thickness, 1 mm of diameter) with a distance of 2.5 mm were deposited on the top surface by thermal evaporation under high vacuum through a shadow mask. The I-V curves were measured using a digital sourcemeter (Keithley 2450). The XRD patterns were collected using a Rigaku (Dmax 2500) X-ray diffractometer equipped with a Cu Kα X-ray (λ = 1.54186 Å) tubes operated at 40 kV and 200 mA. Considering the sensitivity of MSCs towards humidity, we installed the MSC in an optical cryostat under high vacuum (10⁻⁵ Torr) for the series of measurements. We found that vacuum can effectively protect samples from degradation as a result of moisture and other environmental factors (Figure S2).

**Temperature-dependent Vis-NIR PC and R spectroscopy.** For optical interband excitation, a supercontinuum laser source (Fianium, WhiteLase™ SC450-4) combined with a monochromator is used, providing excitation source with wavelengths in the range of 450 nm to 1750 nm. The supercontinuum laser provides 5 ps pulses with a repetition rate of 40 MHz and an average power of 4 W. After the monochromatic light with a linewidth of 1.5 nm goes through a chopper, the Gaussian profile light spot with a diameter of about 2 mm irradiates at the central line between two electrodes with a
power of about 0.3 mW at 840 nm. The photoconductivity signals, PC, are obtained by applying a dc-electric field between the two electrodes and detecting the PC via a preamplifier and then is recorded by a lock-in amplifier in phase with a mechanically chopper (the reference frequency is 220 Hz). Meanwhile the reflected beam from the sample, after passing through the optical lens, is directed to be focused onto a silicon detector. The reflectivity signals, R, are detected by another lock-in amplifier which is referenced by the same chopper at the same time. A highly refined silver mirror was used as the standard (average reflectance is about 95%) to generated reflectance spectrum. To obtain the temperature-dependent photoconductivity and reflectance spectra, the sample was mounted into an optical cryostat (10⁻⁵ Torr), allowing the variation of the temperature in the range of 78-350 K. We found that vacuum can effectively protect samples from degradation as a result of moisture and other environmental factors.

**Temperature-dependent PL spectroscopy.** For variable-temperature continuous wave (CW) PL measurements, a frequency-doubled mode-locked Ti: Sapphire laser (440 nm, 4.5 mW) was applied to serve as excitation source. The sample was mounted on a cold finger of a closed-cycle helium refrigerator (10⁻⁷ Torr) and the sample temperature could be controlled in the range of 8-350 K. The PL was dispersed by a vacuum monochromator and detected by a photomultiplier tube for CW measurements.

**Pump-probe PC spectroscopy.** The pump-probe PC spectroscopy was set up by adding a pump light on the base of the Vis-NIR PC spectroscopy. The changes of PC response of the sample were induced by a photon energy dependent pump light. The pump light was carried out by employing a Ti:sapphire laser with spectral width of 10
nm and a repetition rate of 80 MHz. The excitation wavelength of the pump beam was continually tuned from 680 nm to 1080 nm. The sample is also mounted in an optical cryostat under vacuum (10^{-5} Torr), allowing the variation of the temperature.

### RESULTS AND DISCUSSIONS

**Characterization of MSCs.** First, we used a solution-processed method to obtain MSCs and the according X-ray diffraction (XRD) pattern is given in Figure 1a (black curve), where two main peaks from the same crystal plane (200) and (400) are presented. This indicates that MSC orients mainly along (100) direction parallel to the substrate.\(^9\) Powder XRD pattern of the ground crystals (red curve) demonstrates a pure perovskite phase for MSC. This photograph of MSC indicates the single crystal nature of the resultant and the according configuration is dodecahedron (inset of Figure 1a), a typical crystal habit of a body-centered tetragonal lattice, in agreement with the reported structure at room temperature (space group \(I4/mcm\)).\(^{20}\) The surface properties of MSC is shown in Figure S3. We can conclude that the MSCs have no other impurity elements and the average roughness of surface is about 70 nm from the X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscope (AFM).

Normalized PC (black curve, the electric field is 32 V/cm) and PL spectra (red curve) of the MSC with the incident light perpendicular to sample (\(\theta = 0^\circ\)) at room temperature are given in Figure 1b. The incident angle (\(\theta\)) of excitation light is defined as the angle between the incident light and the out-of-plane direction of the sample. The location of the PL peak is around 1.58 eV and agrees well with the latest experimental results.\(^{21}\) The PL spectrum displays only one peak while the PC spectrum presents two peaks. Surprisingly, we find a strong PC\(_L\) located at 1.48 eV which is far away from the PL
peak, indicating that the PC\textsubscript{L} signal is not from the separation of excitons whose recombination would induce a PL emission. This PC\textsubscript{L} has never been reported, even though the MSCs have been investigated using temperature-dependent photocurrent spectroscopy. In fact, there indeed is a weak low-energy PC peak which has not ever been noticed by Yoshihiko Kanemitsu et al.\textsuperscript{22} We observed that the light spot on the electrodes in experiments has a great influence on PC spectra (Figure S4). And two rectangular-shaped electrodes in this reference are separated by 50 μm, so we speculate that this is maybe the reason why the PC\textsubscript{L} has not ever been noticed. Meanwhile, The location of the absorption edge (PC\textsubscript{L}) also agrees well with the reference (DR spectrum, 1.48 eV)\textsuperscript{10} and indicates that the photons with the energy around 1.48 eV could be absorbed by the materials and contribute to the generation of PC peak with an extremely low possibility of recombination. This is meaningful for realizing high-efficient photovoltaic devices based on such special materials.

The inset in Figure 1c shows the typical current-voltage (I-V) curves of the MSC in dark and under illumination with 3 mW cm\textsuperscript{-2}. It is apparent that both the dark current and photocurrent increase with the enhancement in voltage. The photocurrent value is three orders of magnitude higher than the dark current value and indicates a high efficiency of generation of e-h pairs by photon absorption. More detailed PC spectra under various electric fields with an incident light perpendicular to sample (θ = 0°) at room temperature are given in Figure 1c. With electric field varying from 0 to 48 V/cm, the peak intensities of PC\textsubscript{H} and PC\textsubscript{L} increase almost linearly while corresponding positions are almost immobile (Figure 1d). All these linear relations indicate that the contact of the electrodes with MSC presents a typical Ohmic feature. At room temperature, no noticeable shift in the position of PC\textsubscript{L} was observed over a range of
excitation powers (Figure S5a), and Figure S5b displays the dependence of PCₐ intensity on the excitation powers recorded. We observed a perfectly linear relationship between the power and the PCₐ intensity, which confirms that the absence of nonradiative recombination at room temperature and excitation power has almost no effect on the spectral shape of the PC spectrum.²³

**Temperature-dependent PC-R and PL spectra.** To get more information on the unusual band structure, series of temperature-dependent spectroscopies was measured. Figure 2 shows the according PC, R and PL spectra of the MSCs under temperatures ranging from 10 K to 300 K. Considering that MAPbI₃ presents a second-order phase transition from tetragonal to cubic phase at circa 330 K,²⁴,²⁵ we place the according spectra in Figure S6 to make the figure display concisely. For the PC and R spectra, all the spectra show a prominent dependence of peak positions on the measuring temperatures, and the positions of two PC peaks are in agreement with those of the two absorption edges in R spectra. Meanwhile, the PL spectra of orthorhombic-MAPbI₃ possess three PL peaks, marked as PLₕ(O), PLₕ(O) and PLₘ(O) (Figure 2e). A new PLₘ(O) peak that appears at 1.6 eV between PLₕ(O) and PLₕ(O) also shows blueshift, which has been observed previously²² when the temperature is below 45 K. In contrast to the orthorhombic phase, the tetragonal-MAPbI₃ possesses only one PL feature, marked as PLₕ(T) (Figure 2f).

To begin with the discussion, we have to determine the energy transition positions in these three sets of spectroscopic measurements. For R spectra, interestingly, we observe that high-energy part is sensitive to the angle (α) between the main reflected light and the test direction of silicon detector while the low-energy part is inert to this angle.
(Figure S7). This indicates that the high-energy part is related to the specular reflection components and the low-energy part is relevant to the diffuse reflection components. Unlike in PC and PL spectra where the transition energy could be determined conveniently using the emission peak position directly, the determination of the onset energy in R spectra becomes complicated, attributing to the two close absorption edges. Herein, we directly define the peak position of RH as the onset energy of high-energy absorption edge due to the obvious peak appearance, and use of RL to obtain the onset energy of low-energy absorption edge. The dotted line indicates the linear extrapolation. As shown in Figure S8, a typical representation of these onset energies obtained from R spectrum at 78 K.

We then summarize the temperature dependences of PC and PL peak energies and R onset energies in Figure 3. The significant variations between 130 K and 150 K are attributed to structural phase transition of MAPbI3 from low-temperature orthorhombic phase to the high-temperature tetragonal phase. Apparent changes related to the second-order phase transition are not observable in Figure 3, but the obvious changes in peak intensity of PC_L at around 300 K could be observed in Figure S9, indicative of an additional change from the tetragonal to cubic phase. The phase transitions of MAPbI3 have been extensively studied, we would not focus on this issue.

In the temperature region lower than 130 K where MSC is in orthorhombic phase, two sets of transition energies, high-energy structure corresponding to PC_H, RH and PL_H and low-energy structure corresponding to PC_L, RL and PL_L coexist. Noticeably, PL_L shows a feature of blueshift while PC_L and RL present a redshift feature. This implicates that the corresponding band edge transition for PL_L emission cannot be the same with
that for PL and RL. The consistent blueshift tendency for PLH, PH and RH points to the same band edge for these transitions. In the temperature region where MSC is in tetragonal phase, though the onset energies change in comparison with those in orthorhombic phase, two sets of transition energies still coexist. Therefore, in high-energy part, the coincident blueshift trend of PLH, PH and RH indicates the same band edge for these transitions. In low-energy region, however, the PLL disappears while PL and RL still show a redshift feature toward the increase in temperature.

The blue shift of PH, PLH and RH towards temperature increasing in both orthorhombic and tetragonal phases is opposite to the well-known Varshni relation, probably due to the relevant change in material structures and the interplay between the electron-phonon renormalization and thermal expansion. Since this observation has been well reported, we would emphasize on temperature evolution of PL, PH, and RH. The PL and RL are always in consistency and both show a redshift evolution with the increase of temperature, in agreement with the Varshni relation of normal inorganic semiconductors perfectly. However, the PL corresponding to PL and RL is not observable. The exciton binding energy of MAPbI3 only has a small value of 30 meV at 13 K and the value decreases to 6 meV at 300 K. The energy discrepancy between PH and PL (ΔPC) varies from 50 meV (160 K) to 100 meV (300 K) and these values are prominently larger than those from excitonic effect measured at room temperature. Additionally, the strong signals of PL and RL also indicate that such energy transition should not be originated from the defect or impurity levels. As shown in Figure S10, the full widths at half-maximum (FWHM) of PLH and PC can be fitted by taking into account the temperature-independent inhomogeneous broadening (Γ0) and the interaction between charge carriers and LO-phonons, described by the Fröhlich...
Besides, the PL spectra of MSCs might be influenced by the photon recycling effect. Therefore, the temperature-dependent $\Gamma_{PC}$ reflects more accurately than the temperature-dependent $\Gamma_{PL}$. The extracted fitting values of these peaks are shown in Table S1, which indicate that not the low-energy structure ($PC_L$) but the high-energy structure ($PL_H$) agrees with the literatures. All these point out that in MAPbI$_3$ there exists a special band structure where the photons can be absorbed and converted to charge carriers efficiently with an extremely low possibility for recombining radioactively. This is crucial to the materials for acquiring a high-efficient photovoltaic effect.

The kinetic model of the absorption and photoluminescence processes. Herein, the coexistence of two sets of transition energies in both crystal phases indicates that this is not governed by the crystal structure and a more fundamental issue like the ionic crystal nature could be responsible for this observation. Thus, the conventional consensus, that MA group does not have any significant contribution to the electronic structure around the band edges and the only role is donating electrons to the Pb-I framework, is not feasible and somewhat inaccurate in calculation. More theoretical investigations suggest that MA molecule rotations, with the consequent dynamical change in the band structure, might be the origin of the slow carrier recombination and the superior power conversion efficiency of MAPbI$_3$ based photovoltaic devices. Dar et al. recently claimed that the two PL peaks are associated with the MA-ordered and MA-disordered domains in MAPbI$_3$, via the density functional theory calculations in combination with molecule dynamics models.
In fact, MA cations play an important role in these anomalous emission characteristics of the lead halide perovskites. For calculating the energy band structures, all the researchers assumed that the PbI$_6$ octahedral is a rigid body, MA only affects the tilting of the iodine octahedron in these theoretical calculations, and the bond length and the bond angle of Pb-I-Pb in the octahedron do not change\textsuperscript{15, 24, 40, 41, 42, 43}. However, due to the electrostatic interactions of MA and the surrounded P-I bond, in reality, the bond length and bond angle of Pb-I-Pb in the octahedron should have some adjustments according to the acentric electrostatic nature of MA cation. Therefore, it is of necessity to consider the change of P-I bond in the different positions of the surrounding MA cation.

Specifically in hybrid perovskites, hydrogen bonding (N-H⋯I) effect between the amine group and the halide ions has been verified both theoretically and experimentally.\textsuperscript{24, 44, 45, 46} In this regard, MA molecule would be immobilized by hydrogen bonds and cannot rotate randomly, herein we call it MA-lock state. The distances between the amine group and the surrounding halide ions should not be the same, and the Pb-I bond length near the amine group becomes shorter due to hydrogen bonding and the Pb-I bond length away from the amine group becomes longer under the MA-lock state. As schematically shown in Figure 4a, the hydrogen bonding between N and I is geometrically coupled to the buckling of the Pb-I-Pb bond and the changing of the Pb-I bond length. Under the low-energy optical absorption, the first direct transition corresponds to the charge transfer from hybridized Pb 6s-I 5p orbital to the Pb 6p orbital, forming weakly bound excitons.\textsuperscript{47, 48, 49} Accordingly, the electronic transition from I atom to Pb atom directly leads to the reduction of electron density on the I site, and thereby reduces its Coulomb interaction with the amine group. This in
turn straightens the Pb-I-Pb bond due to the lattice relaxes, resulting in the MA-unlock state in which the MA molecule turns into the condition of random rotation (Figure 4b). Comparing to the long lifetime of charge carriers (22∼1032 ns),\textsuperscript{8} the vibrational (∼300 fs) and rotational (∼3 ps) motion of the organic cation\textsuperscript{50} are very fast. In this case, the electrostatic forces of MA to all the surrounding Pb-I bonds should be the same, thus the length and angle of all the Pb-I bonds should be equal. Furthermore, MA-unlock state would also immediately turn into MA-lock state once again after carrier recombination or extraction.

Based on the proposed molecular dynamic model, there are two types of Pb-I frameworks under MA-lock state which may correspond to high-energy and low-energy band structures. The corresponding two energy band structures are schematically depicted in Figure 4c. Here, there are two direct band structures with the two conduction bands (CB\textsubscript{H} and CB\textsubscript{L}) corresponding to the two valence bands (VB\textsubscript{H} and VB\textsubscript{L}) in \textit{k}-space, resulting in two absorption peaks. However, under MA-unlock state, only one type of Pb-I framework exists and contributes to one band structure (Figure 4d). In MA-unlock state, the carrier recombination has only one luminescence peak after optical absorption. This nature of the changeable band structure in MSC is responsible to the fact that PL\textsubscript{L} is even not observable.

The feasibility of this model could be verified by the following observations. First, in the presence of changeable band structure, the photo-generated electrons and holes in high-energy band structure have a higher possibility to recombine than the electrons and holes in low-energy band structure due to the disappearance of the low-energy band structure in MA-unlock state. This results in a high PC\textsubscript{L} signal rather than PC\textsubscript{H}. Second,
this model also indicates carrier could relax from the band structure in Figure 4c to the band structure in Figure 4d by absorbing phonon energy. This process reduces all possible carrier recombination rates, which thus contributes to the experimentally observed long carrier lifetime and diffusion length in the hybrid lead halide perovskites. Finally, the kinetics on photo-involved charge transition and transfer are investigated using the pump-probe photoconductivity technique.

The Pump-probe PC spectroscopy. To check the feasibility of this model, we designed a system of Pump-probe PC spectroscopy to monitor the dynamics of charge generation and separation, as shown in inset of Figure 5. Meanwhile, Figure 5 shows the statistical results of the intensity change in PC \(_L\) peak (ΔPC \(_L\), probe light), corresponding to the pump photon energy. The two curves measured at 78 K and 293 K (more temperature-dependent Pump-probe PC spectra are shown in Figure S11), respectively, present a similar contour. Specifically, as the pump light energy is the same as PC \(_L\) peak energy, the attenuation of PC \(_L\) shows the highest level. On the contrary, as the pump light energy is close to PC \(_H\) peak energy, PC \(_L\) signal shows an increasing feature. In the spectroscopic region of PC \(_L\) attenuation, the occupancies for the large number of electron-hole pairs generated by the pump light on the low-energy band edge would push the electrons and holes generated by the probe light to the high-energy band edge (Figure 4c) and thus deteriorate the PC signal around PC \(_L\) peak. In the region of PC \(_L\) enhancement, the large amount of electrons and holes excited by pump light is of high possibility to occupy the vacancy on the high-energy band edge and this would inhibit the transfer of charges generated by the probe light to the high-energy band edge (Figure 4c). In this case, the recombination of e-h (probe light) would be inhibited, resulting in the increasing feature of PC \(_L\). Therefore, the feasibility of our model on the
two energy transition channels has been verified. The existence of another band edge below the “true” band edge reported by many research groups \(^{11,12}\) has been given the definite physical meaning and causes the complicated optical responses. The charge transitions from the exited low-energy channel to the high-energy channel by the assistance of additional photon or phonon could also result in interesting effects of photoluminescence upconversion or laser cooling. The according phenomena have been well reported\(^ {51}\) and our model provides a direct physical support for the observations.

**CONCLUSIONS**

In conclusion, we have studied the optical properties of MSCs by means of PC, R and PL spectra. Although the unusual blue shifts of PC\(_H\), R\(_H\) and PL\(_H\) have been observed previously, this low-energy PC\(_L\) and R\(_L\) peaks and their red shifts are the first discoveries on MSCs. More importantly, the according band structure shows an ignorable possibility of charge recombination. It is envisaged that solar cells made of single-crystalline perovskites will render significantly higher power conversion efficiency, as it offers not only better carrier generation and transport efficiencies, but also a broader light absorption spectrum. This work is essential for further development of highly efficient solar cells and other optoelectronic devices based on organometal halide perovskites.
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■ AUTHOR INFORMATION

Author contributions

W.H. and S.Y. contributed equally to this work. W.H. and Y.C. conceived the experiment and analysed the data. W.H. performed the experiments. S.Y. S.Q. and Z.W. provided CH$_3$NH$_3$PbI$_3$ perovskite single crystals. S.Y., P.L. and W.H. performed device fabrication. W.H., Z.W. and Y. L. wrote the manuscript. All the authors discussed the results and commented on the manuscript.

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Notes

The authors declare no competing financial interests.
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Figure 1 | Basic properties of the MSCs at room temperature (293 K). a, XRD patterns of the large perovskite MSC (black) and the ground powder from large MSC (red) with the photograph of MSC shown in the down-right inset. b, Normalized PC (the electric field is 32 V/cm) and PL spectra of the MSC with the incident light perpendicular to sample. c, Electric field-dependent PC spectra with an incident light perpendicular to sample with the I-V curves of MSC shown in the upper-right inset. d, The statistical results of the peak intensity of $PC_H$ and $PC_L$ from figure 1c.
Figure 2 | Temperature-dependent spectra of the MSC. **a,b,** The normalized PC spectra at different temperatures with an external electric field of 32 V/cm. **c,d,** Normalized R spectra with the incident light oblique incidence to sample ($\theta = 10^\circ$). **e,f,** Normalized PL spectra from 10 K to 300 K. The red (blue) arrow lines in the figure indicate that the peaks exhibit continuous redshifts (blueshifts) as temperature increases. All the spectra are intentionally shifted for ease of viewing.
Figure 3 | The band edge characteristics of MSC. The temperature dependences of PC and PL peak energies and R onset energies. The left inset shows the crystal structure of tetragonal-MAPbI$_3$ phase. The rigid framework consisting of the PbI$_6$ octahedral is also highlighted in the structure.
Figure 4 | Proposed mechanism for the absorption and photoluminescence processes in MSC. (a-b) Molecular dynamics schematic illustrations (not to scale) showing that the MA-lock state under the hydrogen bonding between the amine group and the iodine ion and the MA-unlock state that the MA molecule turn into the random rotation, respectively. (c-d) Proposed band diagram correspond to the MA-lock state and the MA-unlock state for MAPbI₃ single crystal, respectively.
Figure 5 | The Pump-probe PC spectroscopy. Pump light photon energy dependence of the change in PC$_L$ intensity (ΔPC$_L$, probe light) at 78 K (black) and 293 K (red). The upper-left inset shows the schematic diagram of Pump-probe PC spectroscopy.
**SUPPORTING INFORMATION**

Figure S1. The schematic of our PC-R system setup.

Figure S2. The normalized PC spectra of MSC with different storage time at room temperature. The sample is mounted into an optical cryostat under vacuum (10^{-5} Torr), and all the spectra are intentionally shifted for ease of viewing.
Figure S3. The surface properties of MSC. (a) XPS of four MSC samples. The surface of Sample 1 has not undergone any treatment, the Sample 2 is thinned by 0.1 mm and polished along one direction, the Sample 3 is thinned by 1 mm and polished along one direction, and the Sample 4 is fabricated by depositing Au and wiring bonding from Sample 3. (b) The AFM image of the sample 3, and the average roughness of this area is about 70 nm.

Figure S4. The PC spectra of MSC under different light spot sizes. The size of light spot 2 is less than the electrode spacing (red curve), and a small amount of light spot 1 illuminates the electrodes (black curve).
**Figure S5.** Excitation power-dependent PC spectra at room temperature. (a) The PC spectra of MSC under different excitation powers. (b) The statistical results of the peak intensity of $PC_L$ from (a).

**Figure S6.** Temperature-dependent spectra of the MSC measured from 300 to 350 K. (a) The normalized PC spectra at different temperatures with an external electric field of 32 V/cm. (b) The normalized R spectra of the same sample with an oblique light incidence ($\theta = 10^\circ$).
Figure S7. $\alpha$ angle dependence of the normalized R (or DR) spectra of the MSC with the schematic illustration of the geometry of the validation experiment shown in the down-left inset, where $\alpha$ is the angle between the main reflected light and the test direction of Si detector.

Figure S8. A typical representative quantitative estimation of the absorption edge through PC and R spectra of MSC at 78 K.
Figure S9. The temperature dependence of the intensity of PC_L.

Figure S10. FWHMs of the PL_H peak (red circles) and the PC_L peak (black and blue circles) obtained for MAPbI_3 single crystals as functions of temperature. The solid red and blue lines show the fit for the temperature-dependent \( \Gamma_{\text{PL}} \) and \( \Gamma_{\text{PC}} \).
Firstly, we obtained the PC spectrum (see Figure S11a) of the sample without pump light at 78 K (Orthorhombic phase). In this case, we could determine the characteristic energies corresponding to the high-energy structure and low-energy structure of the sample, respectively. Finally, we measured Pump-probe PC spectra (see Figure S11b) under pump light modulation at different photon energies. Similarly, Pump-probe PC spectra (see Figure S11c,d) can also be obtained at 293 K (Tetragonal phase).

**Figure S11.** The Pump-probe PC spectra of the MSC. (a) The PC spectrum of the sample without pump light at 78 K. (b) The PC spectrum induced by different pump lights at 78 K. (c) The PC spectrum of the sample without pump light at 293 K. (d) The PC spectrum induced by different pump lights at 293 K.
Table S1. The extracted fitting values of the linewidth parameters of PL$_H$ and PC$_L$.

Linewidth broadening parameters extracted from fits of \( \Gamma(T) = \Gamma_0 + \gamma_{LO} / \left( e^{E_{LO}/k_B T} - 1 \right) \) to the PL$_H$ and PC$_L$ linewidth data. \( \Gamma_0 \) is the inhomogeneous broadening (the linewidth at 0 K), \( \gamma_{LO} \) is the strength of the LO phonon-charge-carrier Fröhlich coupling and \( E_{LO} \) is the relevant LO phonon energy.

| Fitting Parameters | High-energy Transition (PL$_H$) | Low-energy Transition (PC$_L$) |
|--------------------|---------------------------------|------------------------------|
| \( \Gamma_0 \) (meV) | 20                             | 18                           |
| \( \gamma_{LO} \) (meV) | 200                            | 120                          |
| \( E_{LO} \) (meV) | 25                             | 40                           |