

Giant and Broadband Multiphoton Absorption Nonlinearities of a 2D Organometallic Perovskite Ferroelectric

Maofan Li, Yanming Xu, Shiguo Han, Jinlong Xu,* Zhenda Xie, Yi Liu, Zhiyun Xu, Maochun Hong, Junhua Luo, and Zhihua Sun*

Multiphoton absorption (MPA) has been utilized for important technological applications. High-order multiphoton harvesting (e.g., five-photon absorption, 5PA) exhibits unique properties that could benefit biophotonics. Within this field, perovskite oxide ferroelectrics (e.g., BaTiO₃) enable low-order optical nonlinearities of 2PA/3PA processes. However, it is challenging to obtain efficient, high-order 5PA effects. Herein, for the first time, giant and broadband MPA properties are presented in the 2D hybrid perovskite ferroelectric $(IA)_2(MA)_2Pb_3Br_{10}$ (1; IA = isoamylammonium and MA = methylammonium), where multiphoton-excited optical nonlinearities related to different MPA mechanisms over a broadband range of 550–2400 nm are observed. Strikingly, its 5PA absorption cross-section (σ_5) reaches up to 1.2×10^{-132} cm¹⁰ s⁴ photon⁻⁴ (at 2400 nm), almost 10 orders larger than some state-of-the-art organic molecules and a record-high value among all known ferroelectrics. This unprecedented 5PA effect results from the quantum-confined motif of inorganic trilayer sheets (wells) and organic cations (barriers) in 1. Moreover, its large ferroelectric polarization of 5 μ C cm⁻² could promote modulation of MPA effects under external electric fields. As far as it is known, this is the first report on giant, broadband high-order MPA properties in ferroelectrics, which provides potential, novel electric-ordered materials for next-generation biophotonic applications.

M. Li, S. Han, Y. Liu, Z. Xu, Prof. M. Hong, Prof. J. Luo, Prof. Z. Sun State Key Laboratory of Structural Chemistry Fujian Institute of Research on the Structure of Matter Chinese Academy of Sciences Fuzhou, Fujian 350002, P. R. China E-mail: sunzhihua@fjirsm.ac.cn

M. Li, S. Han, Y. Liu, Z. Xu, Prof. M. Hong, Prof. J. Luo, Prof. Z. Sun Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China Fuzhou, Fujian 350108, P. R. China M. Li, S. Han, Y. Liu School of Chemical Sciences University of Chinese Academy of Sciences Chinese Academy of Sciences Beijing 100039, P. R. China Y. Xu, Dr. J. Xu, Prof. Z. Xie National Laboratory of Solid State Microstructures School of Electronic Science and Engineering Nanjing University Nanjing 210093, P. R. China E-mail: Jku@nju.edu.cn

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.202002972.

DOI: 10.1002/adma.202002972

Multiphoton absorption (MPA) involves the optical nonlinearities from the simultaneous absorption of multiple photons, which excites electrons to high-energy states and their subsequent relaxation emits short-wavelength photons.^[1] Such frequency-upconverted processes exhibit fascinating properties and the potential for utilization in biological imaging, optical communication, and optical data storage.^[2] Particularly, compared with two/three-photon absorption (2PA/3PA) effects, high-order MPA processes (e.g., five-photon absorption, 5PA) exhibit unique properties,^[3] such as high spatial confinement, long penetration depth, and low biological damage. All these features would benefit the newly emerging field of biophotonics. Hence, various families of MPA-sensitive materials have been designed, including organic chromophores,^[4] inorganic nanocrystals,^[5] polymers,^[6] and metal-organic frameworks.^[7] Nonetheless, only a few candidates are capable of providing 5PA properties, but they face great challenges

due to their small MPA cross-sections (σ_i , where i = the number of photons absorbed). Currently, 5PA candidates are extremely lacking; consequently, it is highly urgent to explore new materials with large transition probabilities, e.g., high σ_5 values.^[8]

Recently, multilayered 2D hybrid perovskites, $(A')_2(A)_{n-1}B_nX_{3n+1}$, have attracted substantial interest due to their intriguing optoelectronic properties.^[9] Such 2D hybrid perovskites exhibit dramatic structural tunability, allowing for the rational modulation of their electric, photoelectric, and optical activities by controlling the organic cations present and/or by adjusting the thickness of the inorganic sheets (i.e., the number of perovskite layers, *n*). Alternative arrays of these organic cations and inorganic frameworks create quantum-confined motifs.^[10] Underlying quantum and dielectric confinement effects lead to strong, light-matter interactions between excitonic resonances that demonstrate interesting optical nonlinearities, such as self-phase modulation and rich MPA processes.^[11] It has been theorized that this 2D family enables large 2PA/3PA absorption coefficients,^[12] as exemplified by the following perovskites: (PEA)₂PbI₄ (2PA, 211.5 cm MW⁻¹),^[13] (BA)₂(FA)Pb₂Br₇ (2PA, 5.76×10^3 cm GW⁻¹),^[14] and (BA)₂PbBr₄ (3PA, ≈ 7 cm³ GW⁻²).^[15]

Therefore, we endeavored to assess the potential of 2D multilayered hybrid perovskites with strong 5PA effects.

ADVANCED SCIENCE NEWS _____

Another notable merit of the $(A')_2(A)_{n-1}B_nX_{3n+1}$ perovskites is that they allow for further exploration of ferroelectricity,^[16] due to the large degrees of freedom that allow dynamic motion of their organic cations, which are situated in the interspaces between their inorganic perovskite sheets. The combination of ferroelectric polarization with other optical properties affords a new pathway to developing the next generation of photonic devices.^[17] For instance, multiphoton-induced, photorefractive processes were observed in ferroelectric LiNbO3 crystals,[18] in which the ultrahigh, built-in electric field enhanced charge separation and efficient MPA processes. This light-polarization interaction motivated researchers to study the MPA properties of ferroelectrics, such as 2PA/3PA effects in ferroelectric oxides of BaTiO₃ (at 1.064 µm), SrBiTa₂O₉ (at 1.064 µm), Pb_{0.7}La_{0.3}TiO₃ (at 1064 nm), Ce:BaTiO₃ (at 532 nm), and Bi_{3.15}Nd_{0.85}Ti₃O₁₂ (at 800 nm).^[19] Relying on these low-order, 2PA/3PA nonlinear processes, the multiphoton detectors could perform in a narrow, sub-bandgap region (<1.5 µm). However, to date, reports on ferroelectrics exhibiting high-order 5PA optical nonlinearity are limited, hindering their application to multiphoton harvesting in the broadband range (>1.5 μ m). These unique advantages of the $(A')_2(A)_{n-1}B_nX_{3n+1}$ family, including their strong MPA effects and ferroelectricity,^[20] provide a new design for producing promising, MPA-sensitive candidates.

Herein, we present for the first time the giant and broadband MPA properties of a 2D trilayered hybrid perovskite, $(IA)_2(MA)_2Pb_3Br_{10}$ (1; IA = isoamylammonium and MA = methylammonium), that exhibits strong 2PA to 5PA effects over a wavelength range of 550-2400 nm. Particularly, it has an extremely high σ_5 value of up to 1.2×10^{-132} cm¹⁰ s⁴ photon⁻⁴, which is almost ten times larger than that of current, state-ofthe-art organic molecular systems. Spectral dependence of its MPA cross-sections (and the resulting 2PA, 3PA, 4PA, and 5PA effects) revealed its potential for multiphoton detection. Furthermore, 1 shows notable ferroelectricity with large, spontaneous polarization (P_s , 5.0 μ C cm⁻²), offering new opportunities to modulate MPA effects through external field. This work on giant 5PA effect of hybrid perovskite ferroelectrics is unprecedented, which opens new prospects toward next-generation multiphoton application.

A temperature-cooling method was applied to an aqueous solution of 1 to obtain bulk crystals (Figure S1, Supporting Information) and their phase purities were verified by powder X-ray diffraction (XRD). The patterns observed matched well with our simulated results (Figure S2, Supporting Information). Variable-temperature structure analyses disclosed that 1 adopts an intriguing 2D Ruddlesden-Popper trilayered perovskite structure at 298 K, where organic MA⁺ cations act as "perovskitizers" that arrange the inorganic perovskite frameworks.^[21] This structure was created by tailoring bulky IA⁺ cations into the cubic 3D prototype of MAPbBr₃ along the planes perpendicular to the crystallographic (100) direction. Consequently, trilayered halometallate [Pb3Br10]. sheets were formed, consisting of corner-sharing PbBr₆ octahedra and featuring (100)-oriented parallel alignments. Organic IA⁺ cations inside the interlayer spaces were oriented head-to-tail, with two, adjacent, staggered organic layers by the (1/2 1/2) dislocation. It is noteworthy that

this alternative array of inorganic perovskite sheets (wells) and organic bilayers (barriers) constructs the quantum-confined architecture of 1, featuring a periodic lattice with perfect translational symmetry along the *a*-axis. The length of the quantum wells was estimated to be ≈17.8 Å (Figure 1a), which suggests that both electrons and holes would be closely confined inside the wells, leading to a strong binding energy for the excitons.^[22] As far as we know, diverse and rich nonlinear optical properties can be expected in 1, such as MPA effects and excitonphoton couplings. Moreover, the organic IA⁺ cations that are located inside the interlayer spaces adopt flexible, chain-like molecular configurations, which provides them with large degrees of freedom for dynamic motion and reorientation. From a structural viewpoint, the molecular dynamics of these organic moieties are the crucial element that breaks the symmetry and promotes ferroelectric polarization, which has been verified by other hybrid perovskites, such as (CA)₂PbBr₄ and (benzylammonium)₂PbCl₄.^[16c,d] Therefore, this class of 2D multilayered hybrid perovskites, with their distinct, quantum-confined structures, represent a new platform for exploring novel multiphoton-harvesting candidates.

For most ferroelectric materials, symmetry breaking that is related to phase transition is indispensable for generating Ps. Differential scanning calorimetry (DSC) measurements revealed that 1 undergoes reversible phase transitions at 305 and 303 K (Curie temperatures, T_Cs) during heating and cooling cycles, respectively. The temperature dependence of the dielectric constant (\mathcal{E}) displays dramatic anomalies around the T_c , coinciding well with the Curie–Weiss law (Figure 2b). The significant λ -type dielectric peaks suggest that a paraelectric-to-ferroelectric phase transition occurs. Additionally, the second harmonic generation (SHG) effect of 1 is clearly observed at room temperature, the intensity of which being 0.2 times as large as that of the KH₂PO₄ (KDP) standard (Figure S3, Supporting Information). Crystallography analyses confirmed the occurrence of symmetry breaking in 1, where the compound exhibited the Aizu notation of 4/mmmFmm2 (Figure 1b),^[23] which lead to four, equivalent P_s directions of [110], [1-10], [-110], and [-1-10]. Above the T_c , in the paraelectric phase (PEP), 1 was tetragonal with the nonpolar space group of I4/mmm (point group of 4/mmm). Both the organic IA+ and MA⁺ cations were disordered with eight orientational populations and were located on the crystallographic mirror plane, which featured highly symmetric molecular configurations (Figure S4, Supporting Information). For the IA⁺ cations between the inorganic perovskite sheets, remote distribution of its flexible isopentyl moieties caused swing-like molecular motions, and the organic MA⁺ cations inside the central cavities possessed a low barrier for the random, molecular reorientation that endowed the atomic disordering. The inorganic PbBr₆ octahedra also adopted a symmetric architecture with Pb–Br–Pb angles of 180°, revealing the flatness of the $[Pb_3Br_{10}]_{\infty}$ perovskite layers. This centrosymmetric packing cancelled out the dipole moment and net electric polarization of the unit cell of 1 in the PEP. Below the T_c , in the ferroelectric phase (FEP), the crystal structure of 1 changed to orthorhombic with the polar space group of $Cmc2_1$ (point group of mm2; Table S1, Supporting Information). Both types of cations became fully ordered, where the NH₃ groups were closely linked to the PbBr₆





Figure 1. Crystal structures of **1**. a) Diagram of the quantum-well motif with alternate arrays of inorganic perovskite frameworks (well) and organic cation bilayers (barrier). b) Symmetry breaking with an Aizu notation of 4/*mmmFmm2* for **1**. Four equivalent polarization directions (green arrowheads) are verified for **1** at PEP, which coincide with its crystallographic polar *c*-axis at FEP. The pink arrowheads at FEP indicate the distortion of perovskite octahedra.



Figure 2. Ferroelectric and related physical properties of 1. a) DSC traces measured in the heating and cooling runs, disclosing its reversible phase transition at 305/303 K. b) Real part (ε) of the complex permittivity measured along the *c*-axis of single crystal. Inset: the fitting of ε' values by the Curie–Weiss law. c) *P*–*E* hysteresis loop and *I*–*E* curve measured at room temperature. d) Temperature dependence of spontaneous polarization (*P*_s). Inset: pyroelectric currents collected in the heating mode.

ADVANCED

www.advmat.de



octahedra via N-H···Br hydrogen bonds. From the packing views (Figure S5, Supporting Information), we observed that the MA⁺ cation alignment inside the inorganic sheets created a dipolar component along the *c*-axis, and the bulky IA⁺ cations exhibited the same orientation. This coherent reorientation of organic moieties favors the shift of positively charged centers in the *c*-direction. Meanwhile, the corner-sharing PbBr₆ octahedra of the [Pb3Br10]~ sheets presented a distorted geometry, which was verified by the components of in-plane and out-ofplane distortion (Figure S5c, Supporting Information).^[24] The tilting of the PbBr₆ octahedra accounted for the displacement of negatively charged centers along the *c*-axis. As a result, the positive and negative charge centers were separated, giving rise to the molecular dipole moment and electric polarization along the *c*-direction. These structural analyses suggest that the order-disorder of the organic IA⁺ and MA⁺ cations renders a driving force that promotes the phase transition of 1, while the emergence of electric polarization causes the reorientation and the tilting motions of the organic and inorganic components, respectively.

Bulk ferroelectricity of **1** was confirmed by pyroelectric and ferroelectric measurements at room temperature. As shown in Figure 2c, the current versus electric field (*I*–*E*) curve and the spontaneous polarization versus electric field (*P*–*E*) hysteresis loop revealed that the electric polarization of **1** could be switched by an external field, which gave a P_s value of 5.0 μ C cm⁻². This figure of merit is on par with

that of other hybrid perovskite ferroelectrics,^[25] such as (S)-3-*F*-(pyrrolidinium)CdCl₃ (5.79 μ C cm⁻¹), (C₄H₁₀N)CdCl₃ (4.7 μ C cm⁻²), 3-(fluoropyrrolidin-ium)MnCl₃ (5.0 μ C cm⁻²), and (3-ammoniopyrrolidinium)RbBr3 (2.0 µC cm⁻²). However, it is interesting that the coercive field (E_c) for 1 was ≈ 0.8 kV cm⁻¹, which was determined from the P = 0 intercept (Figure 2c). This figure is much smaller than those of pure organic ferroelectrics and polymers, such as croconic acid (11-37 kV cm⁻¹), VDF oligomers (≈1200 kV cm⁻¹), and Nylon-11 (≈600 kV cm⁻¹).^[26] In fact, it is the smallest field that has switched the electric polarization of bulk ferroelectrics at room temperature. Figure 2d depicts the temperature dependence of the polarization of 1, which was obtained by integrating pyroelectric currents with respect to time (inset of Figure 2b). The calculated P_s value was $\approx 6.1 \,\mu\text{C cm}^{-2}$ at 298 K, which was slightly higher than that deduced from the P-E hysteresis loops (Figure S6, Supporting Information). Combining these results with the symmetry breaking of 4/mmmFmm2 and the DSC and dielectric properties, we confirmed that 1 should be a room-temperature ferroelectric material, whose dielectric and quantum confinement effects could enable strong multiphoton harvesting.

Compared with oxide perovskite ferroelectrics (e.g., BaTiO₃), the unique, 2D, quantum-confined motif of **1** permits relatively strong quantum confinement effects and diverse optical properties.^[27] **Figure 3**a presents the linear optical absorption spectrum of **1** where an optical bandgap energy (E_g) of



Figure 3. a) Optical absorption and PL spectra of 1. Inset: Time-resolved PL results with the triexponential decay. b) Electronic band structure calculated by the DFT method. c) Molecular local density of states at CBM and VBM, and the energy-level scheme evidencing its type-I quantum structure.





≈2.3 eV (Figure S7, Supporting Information) was observed, which correlates with our simulated results (Figure 3b). Studies on the electronic band structure and band alignment of 1 disclosed that the valence band maximum (VBM) relates to the Br-4p state, while the conduction band minimum (CBM) originates from Pb-5p states (Figure 3c). This finding reveals a crucial contribution from the perovskite blocks to its natural Type-I quantum wells, for which the thickness is typically on the order of L_{OW} (nm) = 1.78 ($\approx n \times 0.6$).^[28] This suggests that the electrons and holes are strongly confined inside the wells (Figure 3c). As expected, 1 exhibited a sharp photoluminescence (PL) peak around 522 nm (excited by 405 nm; Figure 3a), and the triexponential fitting of the decay trace gave three lifetime components of 48.6, 168.8, and 738.6 ns. The single PL emission with these long decay lifetimes revealed that the relaxation process of 1 is closely involved with an enhanced recombination of excitons,^[29] which would fulfill its MPA activities.

To study the MPA effects of 1, we performed multiphotonexcited PL measurements on thin crystal flakes using a Ti:sapphire femtosecond laser (100 fs, full-width at half maximum; repetition rate of 1 kHz) as the excitation source. Crystal flakes were positioned on the laser focal plane with the beam prolongating along its crystallographic *c*-axis. Upon laser illumination of different excitation wavelengths (1000, 1500, 1700, and 2400 nm), all the multiphoton-excited, upconverted, PL emission spectra of 1 were seen to follow quite similar patterns that were centered at 529 nm (Figure 4). A small redshift (≈7 nm) of the one-photon-excited PL peak was ascribed to the reabsorption effect.^[30] The excitation-energy dependence of PL signals shows linear relationships (insets of Figure 4), and the fitting of the experimental data yielded an intensity dependence of *In*, where n = 2.0, 3.4, 4.1, and 5.1, that corresponded to themechanisms of 2PA, 3PA, 4PA, and 5PA, respectively. Further, its absorption coefficients and σ_i values for the different MPA effects were determined from the nonlinear transmission from the Z-scan results (Figures S10-S12, Supporting Information). The 2PA coefficient (β , 2.1 × 10³ cm GW⁻¹) falls in the range of other 2D hybrid perovskites, $^{[13,31]}$ such as $(BA)_2(MA)Pb_2I_7$ (0.2-0.64 cm MW⁻¹). In comparison with oxide perovskites



Figure 4. Multiphoton absorption properties of 1. a–d) MPA-induced upconverted PL spectra of 2PA, 3PA, 4PA, and 5PA processes upon different wavelength excitations. e) Inverse transmission as a function of laser intensities for 5PA process (λ = 2400 nm), showing the strong saturated absorption. Inset: Z-scan data (blue point) and fitting curve (red). f) Energy diagram and PL photograph of crystal flakes during the 5PA process.





(Table S8, Supporting Information),^[3b,32] this value for 1 is almost two orders of magnitude larger than that of BaTiO₃ films (51.7 cm GW⁻¹), BiFeO₃ (16 cm GW⁻¹), and Ce:BaTiO₃ (59.3 cm GW⁻¹), and is on par with those of CdSe nanocrystals $(10.3 \times 10^3 \text{ cm GW}^{-1})$ and MoS₂ monolayers (7.62 × 10³ cm GW⁻¹). Furthermore, 1 exhibited an ultrahigh σ_5 value of up to 1.2×10^{-132} cm¹⁰ s⁴ photon⁻⁴ (at 2400 nm), which is almost ten times larger than that of conventional organic systems (Table S8, Supporting Information). To the best of our knowledge, this is the first report on the 5PA properties of hybrid perovskite ferroelectrics. Figure 4f shows the energy diagram for the 5PA process of 1. Upon laser illumination (~2400 nm), the 5PAexcitons (i.e., electron-hole pairs) are formed by simultaneous absorption of five mid-infrared (mid-IR) photons, of which the total energy is large enough to overcome the bandgap between the ground state (S_0) and the excited state (S_i) . Subsequently, the interband decay to the lower excitonic state (S₁) results in the MPA-excited PL emission around 530 nm. For 1, its strong, 2D, quantum-confined structure favors the efficient radiative recombination and giant 5PA activities.

Furthermore, we measured the temperature dependence of the 5PA-related PL activities of 1. We found that the PL intensities demonstrate remarkable changes during the phase transition, and the PL intensities in the FEP are much higher than those seen in the PEP (Figure S13, Supporting Information). This temperature-dependent behavior is similar to that of the electric polarization (Figure 2d), which likely relates to the structural changes, including the ordering of organic cations and the distortion of the inorganic PbBr₆ octahedra. These intriguing MPA attributes of 1 highlight its potential for nonlinear optics and bioimaging applications in the broadband range of 550-2500 nm, depending on the different MPA-excited mechanisms. For instance, effective photodetection can be expected from the 4PA-based devices that can perform in the range of 1550-2100 nm, coinciding with the spectral window of fiber-optical communication. Particularly, the giant σ_5 value for the high-order 5PA process of 1 could directly convert the near-IR light of 2100-2600 nm to shortwavelength, visible PL spectra. Such MPA properties of 1 also allow it to take part in multiphoton upconversion lasing, where its unique merits would promote breakthroughs in diverse, laser-based applications.

We have reported the first hybrid perovskite ferroelectric that shows giant MPA effects over a broadband range of 550–2400 nm. Strikingly, its σ_5 value of $\approx 1.2 \times 10^{-132}$ cm¹⁰ s⁴ photon⁻⁴ is record-high among those of all known ferroelectrics, and is about ten times larger than those of most state-ofthe-art organic molecules. This unprecedented 5PA behavior relates to the strong quantum-confinement effect that 1 has on the excitons within its inorganic perovskite frameworks, and the ordering of the organic barrier that triggers its ferroelectricity. Concerning the coupling between light and spontaneous polarization, the presence of ferroelectricity in 1 offers new possibilities relating to modulating MPA effects through external electric fields; however, this concept still requires further investigation. This work provides a novel, photoactive ferroelectric candidate in the family of hybrid perovskites that can be applied to multiphoton applications over broadband ranges.

Experimental Section

Synthesis: Compound 1 was synthesized in a concentrated HBr solution that contained a stoichiometric ratio of PbCO₃, $(CH_3)_2CH(CH_2)_2NH_3Br$, and CH_3NH_3Br . A subsequent temperature-cooling method grew bulk crystals with sizes up to $18.8 \times 6.5 \times 2.1$ mm³.

Physical Properties Measurements: The DSC, SHG, dielectric, and pyroelectric current measurements are described in the Supporting Information. The P-E hysteresis loops were measured on thin crystal plates with a thickness of ≈ 0.5 mm using the double-wave method. Z-scan experiments were performed on thin wafers to measure the σ_i (i = 2, 3, 4, 5) values, with a commercial, femtosecond optical parametric chirped-pulse amplification (OPCPA) laser system (Libra, Coherent; ≈100 fs, 1 kHz) as the beam source (Figure S8, Supporting Information). The light beam was linearly polarized with a focused spot diameter of \approx 200 μ m. Governed by different-frequency, nonlinear mechanisms in OPCPA, the short wavelengths, ranging from 800 to 1600 nm, are signal waves with horizontal polarization, while the long wavelengths in the range of 1500-2400 nm are idler waves with vertical polarization. The crystal wafers were repeatedly rotated to ensure consistency between their *a*-axis and the polarization direction for all the excitation wavelengths (Figure S9, Supporting Information).

As the nonlinear optical properties, the MPA processes can be theoretically described by the following expression

$$\frac{\mathrm{d}I(z)}{\mathrm{d}z} = -\alpha I(z) - \beta I^2(z) - \gamma I^3(z) - \delta I^4(z) - \varphi I^5(z) - \cdots$$
(1)

where I(z) is the intensity of incident light beam propagating along the *z*-axis direction, and *z* is the propagation distance in the flakes. The parameters α , β , γ , δ , and φ are one-, two-, three-, four-, and five-photon nonlinear absorption coefficients, respectively. Here, 5PA nonlinear optical process was taken as an example to elucidate the experiments. At a given photon frequency (f = 2400 nm), only the 5PA process satisfying Equation (1) is available, then the following relationship can be obtained

$$\frac{\mathrm{d}I(z)}{\mathrm{d}z} = -\varphi I^5(z) \tag{2}$$

The solution to this equation is
$$I(z) = \frac{I_0}{[1 + 4\varphi z I_0^4]^{1/4}}$$
 (3)

When $z = L_0$, the nonlinear transmissivity (*T*) of a five-photon absorbing material can be expressed as

$$T = \frac{I(L_0)}{I_0} = \frac{1}{\left[1 + 4\varphi L_0 I_0^4\right]^{1/4}}$$
(4)

where I_0 is the intensity of incident light and L_0 is the optical path length. Hence, φ value can be determined experimentally by measuring the value of *T* at a given level of I_0 , and the 5PA cross-section (σ_5) value can be calculated according to the following equation

$$\sigma_5 = \frac{(h\nu)^4 \varphi}{N_{\text{crystal}}} \tag{5}$$

where $N_{crystal}$ is the molecular density (in units of cm⁻³) of hybrid perovskites. Similarly, the respective absorption coefficients and absorption cross-sections values for 2PA, 3PA, and 4PA can be experimentally determined on the basis of Equation (1). Their detailed values are presented in **Table 1**, which are also compared with other materials in Table S8 in the Supporting information.

X-Ray Crystallographic Determinations: Variable-temperature single crystal diffraction data were collected on an Agilent Technologies SuperNova Dual Wavelength CCD diffractometer at 280 and 330 K, respectively. Data reduction and multiscan absorption correction were performed using the CrysAlisPro software. All crystal structures were solved with the direct method and refined by the Shelx software. Nonhydrogen atoms were refined in anisotropic mode and hydrogen positions were generated in the geometrical mode. CCDC 1968016 and 1968018 contain the supplementary crystallographic data that can

SCIENCE NEWS _____ www.advancedsciencenews.com

DVANCED



Table 1. Multiphoton absorption properties of 1 measured by the femtosecond laser excitation with different excitation wavelengths.

| Multiphoton process | Excitation wavelength [nm] | Absorption coefficient | Absorption cross-section (ơi) |
|---------------------|----------------------------|---|--|
| 2PA | 1000 | eta = 2061.6 cm GW $^{-1}$ | $\sigma_2 = 4.1 \times 10^4 \text{ GM}$ |
| 3PA | 1500 | $\gamma = 1279.2 \text{ cm}^3 \text{ GW}^{-2}$ | $\sigma_{\!3}=2.0\times10^{-74}~\text{cm}^6~\text{s}^2~\text{photon}^{-2}$ |
| 4PA | 2000 | δ = 651.0 cm ⁵ GW ⁻³ | σ_4 = 6.4 $	imes$ 10 ⁻¹⁰³ cm ⁸ s ³ photon ⁻³ |
| 5PA | 2400 | φ = 23.1 cm ⁷ GW ⁻⁴ | $\sigma_{\rm 5}$ = 1.2 × 10 ⁻¹³² cm ¹⁰ s ⁴ photon ⁻⁴ |

be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

M.L. and Y.X. contributed equally to this work. This work was supported by NSFC (21622108, 21875251, 21833010, 21525104, 21971238, 21975258, 61975207, and 21921001), NSF of Fujian Province (2018H0047), the Key Research Program of Frontier Sciences of CAS (ZDBS-LY-SLH024), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB20010200), and the Youth Innovation Promotion of CAS (Y201851). J.X. thanks the National Key R&D Program of China (20219YFA07055000; 2017YFA0303700), Leading-edge Technology Program of Jiangsu Natural Science Foundation (BK20192001), and NSFC (11774161 and 51890861).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D ferroelectrics, five-photon absorption, organometallic perovskites

Received: May 2, 2020 Revised: June 21, 2020 Published online:

- R. L. Sutherland, Handbook of Nonlinear Optics, Marcel Dekker, New York 2003, Ch. 9.
- [2] a) P. N. Prasad, Introduction to Biophotonics, Wiley, New York 2003; b) N. G. Horton, K. Wang, D. Kobat, C. G. Clark, F. W. Wise, C. B. Schaffer, C. Xu, Nat. Photonics 2013, 7, 205.
- [3] a) Q. Zheng, H. Zhu, S.-C. Chen, C. Tang, E. Ma, X. Chen, Nat. Photonics 2013, 7, 234; b) W. Chen, S. Bhaumik, S. A. Veldhuis, G. Xing, Q. Xu, M. Grätzel, S. Mhaisalkar, N. Mathews, T. C. Sum, Nat. Commun 2017, 8, 15198.
- [4] M. Albota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu, C. Xu, *Science* **1998**, *281*, 1653.
- [5] D. R. Larson, W. R. Zipfel, R. M. Williams, S. W. Clark, M. P. Bruchez, F. W. Wise, W. W. Webb, *Science* **2003**, *300*, 1434.
- [6] C. Bauer, B. Schnable, E. B. Kley, U. Scherf, H. Giessen, R. F. Mahrt, Adv. Mater. 2002, 14, 673.

- [7] H. S. Quah, W. Chen, M. K. Schreyer, H. Yang, M. W. Wong, W. Ji, J. J. Vittal, *Nat. Commun.* **2015**, *6*, 7954.
- [8] H. H. Fan, L. Guo, K. F. Li, M. S. Wong, K. W. Cheah, J. Am. Chem. Soc. 2012, 134, 7297.
- [9] a) L. Dou, A. B. Wong, Y. Yu, M. Lai, N. Kornienko, S. W. Eaton, A. Fu, C. G. Bischak, J. Ma, T. Ding, N. S. Ginsberg, L.-W. Wang, A. P. Alivisatos, P. Y. Yang, *Science* 2015, 349, 1518; b) H. Tsai, W. Nie, J.-C. Blancon, C. C. Stoumpos, R. Asadpour, B. Harutyunyan, A. J. Neukirch, R. Verduzco, J. J. Crochet, S. Tretiak, L. Pedesseau, J. Even, M. A. Alam, G. Gupta, J. Lou, P. M. Ajayan, M. J. Bedzyk, M. G. Kanatzidis, A. D. Mohite, *Nature* 2016, 536, 312; c) D. Jariwala, T. J. Marks, M. C. Hersam, *Nat. Mater.* 2017, 16, 170.
- [10] a) K. Tanaka, T. Kondo, Sci. Technol. Adv. Mater. 2003, 4, 599; b) J.-C. Blancon, A. V. Stier, H. Tsai, W. Nie, C. C. Stoumpos, B. Traoré, L. Pedesseau, M. Kepenekian, F. Katsutani, G. T. Noe, J. Kono, S. Tretiak, S. A. Crooker, C. Katan, M. G. Kanatzidis, J. J. Crochet, J. Even, A. D. Mohite, Nat. Commun. 2018, 9, 2254; c) A. Miyata, A. Mitioglu, P. Plochocka, O. Portugall, J. T.-W. Wang, S. D. Stranks, H. J. Snaith, R. J. Nicholas, Nat. Phys. 2015, 11, 582.
- [11] I. Abdelwahab, P. Dichtl, G. Grinblat, K. Leng, X. Chi, I.-H. Park, M. P. Nielsen, R. F. Oulton, K. P. Loh, S. A. Maier, *Adv. Mater.* 2019, *31*, 1902685.
- [12] a) K. F. Mak, S. Jie, Nat. Photonics 2016, 10, 216; b) F. Zhou, W. Ji, Opt. Lett. 2017, 42, 3113; c) F. Zhou, J. H. Kua, S. Lu, W. Ji, Opt. Express 2018, 26, 16093.
- [13] W. Liu, J. Xing, J. Zhao, X. Wen, K. Wang, P. Lu, Q. Xiong, Adv. Opt. Mater. 2017, 5, 1601045.
- [14] L. Li, X. Shang, S. Wang, N. Dong, C. Ji, X. Chen, S. Zhao, J. Wang, Z. Sun, M. Hong, J. Luo, J. Am. Chem. Soc. 2018, 140, 6806.
- [15] S. Lu, F. Zhou, Q. Zhang, G. Eda, W. Ji, Adv. Sci. 2019, 6, 1801626.
- [16] a) L. Li, Z. Sun, P. Wang, W. Hu, S. Wang, C. Ji, M. Hong, J. Luo, Angew. Chem., Int. Ed. 2017, 56, 12150; b) Z. Wu, X. Liu, C. Ji, L. Li, S. Wang, Y. Peng, K. Tao, Z. Sun, M. Hong, J. Luo, J. Am. Chem. Soc. 2019, 141, 3812; c) W.-Q. Liao, Y. Zhang, C.-L. Hu, J.-G. Mao, H.-Y. Ye, P.-F. Li, S. D. Huang, R.-G. Xiong, Nat. Commun. 2015, 6, 7338; d) S. Han, X. Liu, Y. Liu, Z. Xu, Y. Li, M. Hong, J. Luo, Z. Sun, J. Am. Chem. Soc. 2019, 141, 12470.
- [17] a) J. Kreisel, M. Alexe, P. A. Thomas, Nat. Mater. 2012, 11, 260; b) S. Y. Yang, J. Seidel, S. J. Byrnes, P. Shafer, C. H. Yang, M. D. Rossell, P. Yu, Y. H. Chu, J. F. Scott, J. W. Ager, L. W. Martin, R. Ramesh, Nat. Nanotechnol. 2010, 5, 143; c) I. Grinberg, D. V. West, M. Torres, G. Y. Gou, D. M. Stein, L. Y. Wu, G. N. Chen, E. M. Gallo, A. R. Akbashev, P. K. Davies, J. E. Spanier, A. M. Rappe, Nature 2013, 503, 509; d) H.-Y. Ye, W.-Q. Liao, C.-L. Hu, Y. Zhang, Y.-M. You, J.-G. Mao, P.-F. Li, R.-G. Xiong, Adv. Mater. 2016, 28, 2579.
- [18] P. Günter, J.-P. Huignard, Photorefractive Materials and Their Applications II: Survey of Applications, Springer-Verlag, New York 1989.
- [19] a) Q. C. Zhao, Y. Liu, W. S. Shi, W. Ren, L. Y. Zhang, X. Yao, *Appl. Phys. Lett.* **1996**, *69*, 458; b) W. F. Zhang, M. S. Zhang, Z. Yin, Y. Z. Gu, Z. L. Du, B. L. Yu, *Appl. Phys. Lett.* **1999**, *75*, 902; c) W. F. Zhang, Y. B. Huang, M. S. Zhang, Z. G. Liu, *Appl. Phys. Lett.* **2000**, *76*, 1003; d) S. Li, X. L. Zhong, G. H. Cheng, X. Liu, J. B. Wang, J. Huang, H. J. Song, C. B. Tan, B. Li, Y. C. Zhou, *Appl. Phys. Lett.* **2014**, *105*, 192901.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com



- [20] C. Katan, N. Mercier, J. Even, Chem. Rev. 2019, 119, 3140.
- [21] B. Saparov, D. B. Mitzi, Chem. Rev. 2016, 116, 4558.
- [22] a) Y. Xu, Q. Chen, C. Zhang, R. Wang, H. Wu, X. Zhang, G. Xing, W. W. Yu, X. Wang, Y. Zhang, M. Xiao, *J. Am. Chem. Soc.* 2016, 138, 3761; b) Z. Guo, X. Wu, T. Zhu, X. Zhu, L. Huang, ACS Nano 2016, 10, 9992.
- [23] K. Aizu, Phys. Rev. B 1970, 2, 754.
- [24] B. Traore, L. Pedesseau, L. Assam, X. Che, J.-C. Blancon, H. Tsai, W. Nie, C. C. Stoumpos, M. G. Kanatzidis, S. Tretiak, A. D. Mohite, J. Even, M. Kepenekian, C. Katan, ACS Nano 2018, 12, 3321.
- [25] a) Y. Tang, Y. Ai, W. Liao, P. Li, Z. Wang, R.-G. Xiong, Adv. Mater. **2019**, 31, 1902163; b) W. Xu, C. He, C. Ji, S. Chen, R. Huang, R. Lin, W. Xue, J. Luo, W. Zhang, X. Chen, Adv. Mater. **2016**, 28, 5886; c) W. Liao, Y. Tang, P. Li, Y. You, R.-G. Xiong, J. Am. Chem. Soc. **2017**, 139, 18071; d) H. Zhang, X. Song, H. Cheng, Y. Zeng, Y. Zhang, P. Li, W. Liao, R.-G. Xiong, J. Am. Chem. Soc. **2020**, 142, 4604.
- [26] S. Horiuchi, Y. Tokura, Nat. Mater. 2008, 7, 357.

- [27] a) G. C. Papavassiliou, I. B. Koutselas, A. Terzis, M.-H. Whangbo, Solid State Commun. 1994, 91, 695; b) D. B. Mitzi, K. Chondroudis, C. R. Kagan, IBM J. Res. Dev. 2001, 45, 29; c) M. E. Kamminga, H.-H. Fang, M. R. Filip, F. Giustino, J. Baas, G. R. Blake, M. A. Loi, T. T. M. Palstra, Chem. Mater. 2016, 28, 4554.
- [28] J. Even, L. Pedesseau, C. Katan, ChemPhysChem 2014, 15, 3733.
- [29] a) T. Goto, H. Makino, T. Yao, C. H. Chia, T. Makino, Y. Segawa, G. A. Mousdis, G. C. Papavassiliou, *Phys. Rev. B: Condens. Matter Mater. Phys.* 2006, 73, 115206; b) X. Chen, H. Lu, Z. Li, Y. Zhai, P. F. Ndione, J. J. Berry, K. Zhu, Y. Yang, M. C. Beard, ACS Energy Lett. 2018, 3, 2273.
- [30] Y. Wang, V. D. Ta, Y. Gao, T. C. He, R. Chen, E. Mutlugun, H. V. Demir, H. D. Sun, Adv. Mater. 2014, 26, 2954.
- [31] F. Zhou, I. Abdelwahab, K. Leng, K. P. Loh, W. Ji, Adv. Mater. 2019, 31, 1904155.
- [32] a) B. Gu, Y. Wang, J. Wang, W. Ji, *Opt. Express* 2009, *17*, 10970;
 b) Y. Li, N. Dong, S. Zhang, X. Zhang, Y. Feng, K. Wang, L. Zhang, J. Wang, *Laser Photonics Rev.* 2015, *9*, 427.