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Introduction

Nonlinear optical (NLO) materials, particularly second harmonic generation (SHG) crystals, offer effective ways for tuning the laser wavelength and expanding its spectral range.¹⁻⁶ Traditionally, high-quality second-order NLO crystals must satisfy several fundamental conditions, such as exhibiting a noncentrosymmetric structure, possessing a strong SHG effect, having a wide bandgap and transmission window, featuring appropriate birefringence for phase matchability, and having a conducive crystal growth method.⁷⁻¹⁰ To date, several commercialized NLO crystals have been used, including KBe₂-BO₃F₂ (KBBF), β -BaB₂O₄ (BBO), KH₂PO₄ (KDP), KTiOPO₄ (KTP), AgGaS₂ (AGS), and α -LiIO₃.

Over the past few years, interest in the development of semiorganic NLO crystals has been steadily increasing. These crystals feature many advantages such as the availability of a wide

From $H_{12}C_4N_2CdI_4$ to $H_{11}C_4N_2CdI_3$: a highly polarizable CdNI₃ tetrahedron induced a sharp enhancement of second harmonic generation response and birefringence[†]

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In this study, we identify a novel class of second-order nonlinear optical (NLO) crystals, non- π -conjugated piperazine (H₁₀C₄N₂, PIP) metal halides, represented by two centimeter-sized, noncentrosymmetric organic-inorganic metal halides (OIMHs), namely H₁₂C₄N₂Cdl₄ (*P*2₁2₁2₁) and H₁₁C₄N₂Cdl₃ (*Cc*). H₁₂C₄N₂Cdl₄ is the first to be prepared, and its structure contains a Cdl₄ tetrahedron, which led to a poor NLO performance, including a weak and non-phase-matchable second harmonic generation (SHG) response of 0.5 × KH₂PO₄ (KDP), a small birefringence of 0.047 @1064 nm and a narrow bandgap of 3.86 eV. Moreover, H₁₂C₄N₂Cdl₄ is regarded as the model compound, and we further obtain H₁₁C₄N₂Cdl₃ *via* the replacement of Cdl₄ with a highly polarizable CdNl₃ tetrahedron, which results in a sharp enhancement of SHG response and birefringence. H₁₁C₄N₂Cdl₃ exhibits a promising NLO performance including 6 × KDP, 4.10 eV, $\Delta n = 0.074$ @1064 nm and phase matchability, indicating that it is the first OIMH to simultaneously exhibit strong SHG response (>5 × KDP) and a wide bandgap (>4.0 eV). Our work presents a novel direction for designing high-performance NLO crystals based on organic-inorganic halides and provides important insights into the role of the hybridized tetrahedron in enhancing the SHG response and birefringence.

range of organic components, tunability of inorganic structures, and ease of single crystal growth.^{11–15} Notably, the compounds containing π -conjugated organic moieties have attracted the most attention, and many promising NLO materials in such classes have been reported, such as KLi(HC₃N₃O₃)·2H₂O (5.3 × KDP),¹¹ Lu₅(C₃N₃O₃)(OH)₁₂ (4.2 × KDP),¹² C(NH₂)₃SO₃F (5 × KDP),¹³ (C₅H₆ON)⁺(H₂PO₄)⁻ (3 × KDP),¹⁴ and [*o*-C₅H₄NHOH]₂[-I₇O₁₈(OH)]·3H₂O (8.5 × KDP).¹⁵ Alongside these compounds, several organic–inorganic metal halides (OIMHs) formed from the combination of a π -conjugated organic cation with a metalhalide polyhedron have also been discovered to show NLO performance, such as (H₇C₃N₆)(H₆C₃N₆)MCl₃ (M = Hg and Zn; 5 × and 2.8 × KDP),^{16,17} [C₁₈H₂₁N₄][AgX₃]X (X = Cl, Br, and I, 6.2, 6.5 and 7.6 × KDP),¹⁸ α -(CN₃H₆)₃Cu₂I₅ (1.8 × KDP),¹⁹ and (C₆H₁₁N₂)PbBr₃ (8 × KDP).²⁰

It is also worth studying the NLO properties of non- π conjugated OIMHs, which is similar to the approach of expanding the chemical system from π -conjugated borates to non- π -conjugated phosphates or sulfates.^{21–27} Traditionally, the introduction of metal cations with stereo-chemically active lone-pair electrons (SCALP cation, *e.g.* Bi³⁺, Pb²⁺, and Ge²⁺) or d¹⁰ transition metal cations (d¹⁰-TM cation, *e.g.* Zn²⁺ and Cd²⁺) can effectively design novel SHG-active non- π -conjugated OIMHs.^{28–34} However, on the one hand, the use of SCLAP cations



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 $[\]dagger$ Electronic supplementary information (ESI) available. CCDC 2264014 and 2264015 for $H_{12}C_4N_2CdI_4$ and $H_{11}C_4N_2CdI_3$. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3sc03052k

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is known to cause red shifts in absorption edges and reduce bandgaps of the resulting crystals, limiting their potential applications in the ultraviolet (UV) and deep-UV regions.³⁵⁻⁴⁰ For instance, Mao's group recently reported a series of Ge²⁺-containing OIMHs, in which (CH₃NH₃)GeBr₃ shows a large SHG response (5.3 \times KDP) but a small bandgap (2.91 eV). There are also similar cases to $C_4H_9NOBiBr_7$ (2.2 × urea, 2.67 eV) and $(C_6H_5(CH_2)_4NH_3)_4BiI_7 \cdot H_2O$ (1.3 × AGS, 2.29 eV).⁴¹ On the other hand, many non- π -conjugated OIMHs with d¹⁰-TM cations, such as (C₄H₁₀NO)₂Cd₂Cl₆,⁴² (L/D-C₁₀H₂₀N₂O₄)₂Cd₅Cl₁₂,⁴³ L/D-C₆H₁₀N₃O₂ZnBr₃,⁴⁴ [C₅H₁₄NO]CdCl₃,⁴⁵ L/D-C₁₂H₂₀N₆O₄Cd₂Cl₅,⁴⁴ and ((CH₃)₃NCH₂Cl)CdCl₃,⁴⁶ usually possess wide bandgaps (>5.0 eV) but relatively weak SHG effects (<1.0 \times KDP). Hence, it is challenging to develop NLO OIMHs that simultaneously exhibit both a strong SHG effect (>5 \times KDP) and wide bandgap (>4.0 eV).

To overcome this challenge, our efforts are focused on the non- π -conjugated organic moiety-Cd²⁺/Zn²⁺-I⁻ system. In the beginning, a noncentrosymmetric OIMH, H₁₂C₄N₂CdI₄, has been hydrothermally prepared. But our experimental results show that this compound has a small bandgap (3.86 eV) along with a weak and non-phase-matchable SHG response (0.5 \times KDP). Such an undesired NLO performance could be attributed to the high symmetry and weak anisotropy of the CdI₄ tetrahedron. To the best of our knowledge, this phenomenon is reminiscent of metal sulfates based on a tetrahedral SO_4^{2-} unit. And in metal sulfates, one effective route to overcome this problem is to partially substitute O atoms in SO_4^{2-} , as seen in LiSO₃F,⁴⁷ Na₁₀Cd(NO₃)₄(SO₃S)₄,⁴⁸ Ba(NH₂SO₃)₂,⁴⁹ Ba(SO₃CH₃)₂,⁵⁰ and so on. Hence, furthermore, H₁₂C₄N₂CdI₄ is regarded as the model compound, and we consider that the coordination of $H_{10}C_4N_2$ with a Cd^{2+} cation could result in the partial substitution of I⁻ anions in the CdI₄ tetrahedron, forming a polarizable Cd-I-N unit, which could enhance the SHG response and birefringence in new OIMHs. Additionally, we also hope that new compound involves a smaller number of I⁻ anions in order to exhibit a wider bandgap. Therefore, a novel OIMH, namely H₁₁C₄N₂CdI₃, is prepared via regulating the synthetic conditions of H₁₂C₄N₂CdI₄ (a lower concentration of I⁻ anions in the reaction system). H₁₁C₄N₂CdI₃ contains a distorted CdNI₃ tetrahedron and demonstrates superior NLO performance in comparison to H₁₂C₄N₂CdI₄. Specifically, H₁₁C₄N₂CdI₃ exhibits a strong and phase-matchable SHG effect (6 \times KDP), large birefringence ($\Delta n = 0.062$ (a)1064 nm), and a wide bandgap (4.10 eV), indicating its potential as a promising ultraviolet NLO material.

Methods

Materials and synthesis

CdO (>99%), Y₂O₃ (>99%), and piperazine (>99%), HI (55–58% wt), were used as purchased from Adamas-beta. There are different synthesis conditions of $H_{12}C_4N_3CdI_4$ and $H_{11}C_4N_2CdI_3$ (Table S1†), and the best conditions (larger size and higher yields) are mentioned as follows. For the preparation of $H_{12}C_4N_2CdI_4$, the starting materials are CdO, (256.8 mg, 2 mmol), piperazine (86.14 mg, 1 mmol), HI (2 mL) and H_2O (1

mL). A mixture of the starting materials was placed in Teflon pouches (23 mL) sealed in an autoclave which was heated at 90 ° C for 72 hours, and cooled to 30 °C at 1.67 °C h⁻¹. Yellow block-shaped crystals of $H_{12}C_4N_2CdI_4$ were obtained in high yields of ~95% (based on Cd). For the preparation of $H_{11}C_4N_2CdI_3$, the starting materials are CdO, (128.4 mg, 1 mmol), Y₂O₃, (112.5 mg, 0.5 mmol), piperazine (172.28 mg, 2 mmol), HI (1 mL) and H₂O (2 mL). A mixture of the starting materials was placed in Teflon pouches (23 mL) sealed in an autoclave which was heated at 110 °C for 72 hours, and cooled to 30 °C at 1.67 °C h⁻¹. Yellow block-shaped crystals of $H_{11}C_4N_2CdI_3$ were obtained in high yields of ~95% (based on Cd).

Single crystal structure determination

Single-crystal X-ray diffraction data for the title compounds were collected on an Xcalibur, Eos, Gemini diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K and a Rigaku XtaLAB Synergy-DW dual-wavelength CCD diffractometer with Cu Ka radiation ($\lambda = 1.54184$ Å) at 109 K. Data reduction was performed with CrysAlisPro, and absorption correction based on the multi-scan method was applied.⁵¹ The structures of H₁₂C₄N₂CdI₄ and H₁₁C₄N₂CdI₃ were determined by the direct methods and refined by full-matrix least-squares fitting on F^2 using SHELXL-2014.52 All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was checked for missing symmetry elements using PLATON, and none were found.53 The Flack parameters refined for $H_{12}C_4N_2CdI_4$ and $H_{11}C_4N_2CdI_3$ are 0.45(12) and -0.01(2), respectively, indicating the correctness of their absolute structures. In addition, twinning was observed in H₁₂C₄N₂CdI₄ and H₁₁C₄N₂CdI₃, and the twin laws of these compounds were (-1.0, 0.0, 0.0, 0.0, -1.0, 0.0, 0.0, 0.0, -1.0) and (-1.0, 0.0, 0.0, 0.0, -1.0, 0.0, 0.0, 0.0, -1.0), respectively. Crystallographic data and structural refinements of the compounds are listed in Tables S2-S6.†

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Ultima IV diffractometer with graphite-monochromated Cu K α radiation in the 2 θ range of 10–70° with a step size of 0.02°.

Thermal analysis

Thermogravimetric analysis (TGA) was performed with a Rigaku TG-DTA 8121 unit under an Ar atmosphere, at a heating rate of 10 °C min⁻¹ in the range from 30 to 800 °C.

Optical measurements

The infrared (IR) spectrum was recorded on a Thermo Fisher Nicolet 5700 FT-IR spectrometer in the form of KBr pellets in the range from 4000 to 400 cm⁻¹.

The ultraviolet-visible-infrared (UV-vis-IR) spectrum in the range of 200–800 nm was recorded on a PerkinElmer Lambda 750 UV-vis-NIR spectrophotometer. The reflectance spectrum was converted into an absorption spectrum by using the Kubelka–Munk function.⁵⁴

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Second harmonic generation measurements

Powder SHG measurements were carried out with a O switch Nd:YAG laser generating radiation at 1064 nm according to the method of Kurtz and Perry.55 Crystalline H12C4N2CdI4 and H₁₁C₄N₂CdI₃ samples were sieved into distinct particle-size ranges (50-70, 70-100, 100-140, 140-200, 200-250 and 250- $325 \,\mu\text{m}$). Sieved KH₂PO₄ (KDP) samples in the same particle-size ranges were used as references.

Elemental analysis

The elemental content was measured on a Vario EL Cube elemental analyzer from Elementar Analysensysteme GmbH, Germany. The combustion temperature was 800 °C (Table S7†).

Energy-dispersive X-ray spectroscopy

Microprobe elemental analyses were performed and the elemental distribution maps were obtained on a field-emission scanning electron microscope (Phenom LE) equipped with an energy-dispersive X-ray spectroscope (EDS, Phenom LE).

Computational method

The electronic structures and optical properties were obtained using a plane-wave pseudopotential method within density functional theory (DFT) implemented in the total energy code CASTEP.56,57 For the exchange and correlation functional, we chose Perdew-Burke-Ernzerhof (PBE) in the generalized gradient approximation (GGA).⁵⁸ The interactions between the ionic cores and the electrons were described by the normconserving pseudopotential.59 The following orbital electrons were treated as valence electrons: I-5s²5p⁵, Cd-4s24p⁶5s², H-1s¹, C-2s²2p² and N-2s²2p³. The numbers of plane waves included in the basis sets were determined at a cutoff energy of 700 eV. During the SCF and optical-property calculations of the two compounds, the k-point separation was set to 0.04 \AA^{-1} to perform the numerical integration of the Brillouin zone, and the corresponding k-point samplings are 3 \times 2 \times 2 and 2 \times 4 \times 2 for H₁₂C₄N₂CdI₄ and H₁₁C₄N₂CdI₃, respectively. After the principal axis transformation, the k-point sampling of $H_{11}C_4N_2CdI_3$ changes to 2 × 3 × 2 when the *k*-point separation is 0.04 \AA^{-1} . The other parameters and convergent criteria were the default values of the CASTEP code.56,57

The calculations of second-order NLO susceptibilities were based on length-gauge formalism within the independent particle approximation.^{60,61} The second-order NLO susceptibility can be expressed as

$$\chi_{abc} L(-2\omega; \omega, \omega) = \chi_{abc} \operatorname{inter} (-2\omega; \omega, \omega) + \chi_{abc} \operatorname{inter} (-2\omega; \omega, \omega) + \chi_{abc} \operatorname{mod} (-2\omega; \omega, \omega)$$

where the subscript *L* denotes the length gauge, and χ_{abc} inter, χ_{abc} intra and χ_{abc} mod give the contributions to χ_{abc} L from interband processes, intraband processes, and the modulation of interband terms by intraband terms, respectively.

The convergence test of the SHG coefficient upon k-point sampling and empty bands with H₁₁C₄N₂CdI₃ as an example

was carried out (Table S9[†]), and we found that the SHG coefficient gradually converges when the k-point separation is not more than 0.04 Å⁻¹ (2 \times 3 \times 2) and the quantity of the empty bands is not less than 2 times that of valence bands (280 bands). So the choice of k-point sampling and the empty band number during the optical property calculation is reasonable.

Results and discussion

In order to investigate the differences in the synthesis conditions of H₁₂C₄N₃CdI₄ and H₁₁C₄N₂CdI₃, we conducted multiple sets of control experiments as shown in Table S1.[†] Several observations were made: (1) the molar ratio of Cd to $H_{10}C_4N_2$ had no impact on whether H₁₂C₄N₃CdI₄ or H₁₁C₄N₂CdI₃ was produced as the final product; (2) changes in temperature had minimal effects on the synthesis of $H_{12}C_4N_3CdI_4$; (3) the ratio of HI to H₂O was the determining factor in the preparation of H₁₂C₄N₃CdI₄ or H₁₁C₄N₂CdI₃. We hypothesize that a lower HI : H₂O ratio can reduce the concentration of iodide ions in the reaction system, thus facilitating direct coordination bonding between Cd^{2+} cations and $H_{10}C_4N_2$, resulting in the formation of H₁₁C₄N₂CdI₃; (4) in the preparation process of H₁₁C₄N₂CdI₃, Y_2O_3 is essential and cannot be omitted. However, indeed, the specific role of Y₂O₃ in the synthesis process of H₁₁C₄N₂CdI₃ is currently unclear due to limitations in our current technological means. Their measured powder XRD patterns are consistent with those of simulated data, confirming the phase purity (Fig. S1[†]). The EDS results of the Cd: I ratios are 1.0: 4.10 and 1.0: 2.97 for $H_{12}C_4N_2CdI_4$ and $H_{11}C_4N_2CdI_3$, respectively (Fig. S2[†]). In addition, elemental analysis of C, N, and H atoms is provided in Table S6[†] with weight%: C 6.77, H 1.63, and N 4.02 for H₁₂C₄N₂CdI₄; C 8.30, H 1.85, and N 4.53 for H₁₁C₄N₂CdI₃ (Table S7[†]). Both of them are in good agreement with the crystal structure solution.

Crystal structure

H₁2C₄N₂CdI₄ crystallizes in a noncentrosymmetric space group $P2_{1}2_{1}2_{1}$ (No. 19) with one cationic $H_{12}C_{2}N_{4}^{2+}$ ($H_{2}PIP^{2+}$) sixmembered ring and one anionic CdI₄²⁻ tetrahedron in each asymmetric unit (Fig. 1). In the H₁₂C₄N₂-ring, each C and N atom exhibits sp3 hybridization, with C-N/C-C distances of 1.49(2)-1.50(2) Å and 1.474(17)-1.496(18) Å, respectively. The bond angles in the H₁₂C₄N₂-ring range from 110.5(12)-111.2(11)°, which is consistent with those of previously reported piperazine compounds.^{62,63} As a result, the H₁₂C₂N₄²⁺ cation takes on a chair conformation, rather than a planar π -conjugated structure. Each Cd²⁺ cation bonds with four I⁻ anions to form a CdI4 tetrahedron, with Cd-I distances ranging from 2.7548(14)-2.8089(14) Å and I-Cd-I angles of 104.50(4)-113.75(5)°. Neighboring H₁₂C₂N₄ and CdI₄ groups are isolated from each other and arranged in a quasi-two-dimensional (quasi-2D) $[H_{12}C_4N_2CdI_4]$ layer (Fig. 1c), parallel to the ac plane. These pseudo-layers stack along the *b* direction to form the entire 3D network of H₁₂C₄N₂CdI₄ (Fig. 1d).

 $H_{11}C_4N_2CdI_3$ crystallizes in the polar space group Cc (No. 9), with an asymmetric unit including one protonated-piperazine **Chemical Science**



Fig. 1 Views of the structures of the Cdl₄ tetrahedron (a), the chair shaped H_2PIP^{2+} cation (b), the quasi-2D $H_{12}C_2N_4Cdl_4$ layer along the *b*-axis (c) and $H_{12}C_2N_4Cdl_4$ along the *a*-axis (d).

group, one Cd, and three I atoms (Fig. 2a). In the chair-shaped $H_{11}C_4N_2$ -ring, C–N and C–C distances are 1.49(2)–1.532(17) Å and 1.462(17)–1.509(19) Å, respectively, and the bond angles are in the range of 108.7(11)–114.5(9)°, which are consistent with those of previously reported piperazine compounds.^{62,63} Each Cd²⁺ cation connects with one N atom and three I atoms to form a *N*-hybrid polyhedron, a CdNI₃ tetrahedron. The length of Cd–N (2.300(11) Å) is smaller than those of Cd–I (2.7393(12)–2.7518(11) Å), and the bond angles of N–Cd–I and I–Cd–I are 100.8(3)–104.0(3)° and 112.80(3)–117.07(4)°, respectively. Furthermore, one $H_{11}C_4N_2$ -ring is connected with one CdNI₃ tetrahedron *via* the corner-sharing of N atoms, forming a H_{11} -C₄N₂CdI₃ molecule (Fig. 2a). Neighboring $H_{11}C_4N_2$ CdI₃ molecules are interconnected in a quasi-1D zigzag chain along the *c*-direction, which is further arranged in quasi-2D layers parallel



Fig. 2 Views of the structures of the $H_{11}C_4N_2CdI_3$ molecule (a), the quasi-2D $H_{11}C_4N_2CdI_3$ layer along the *a*-axis (b) and $H_{11}C_4N_2CdI_3$ along the *b*-axis.

to the *bc* plane (Fig. 2b). These quasi-2D layers are stacked upward along the *a*-axis, resulting in the structure of $H_{11}C_4N_2CdI_3$ (Fig. 2c).

Structural comparison

It is interesting to compare the structural differences of the title compounds to further understand why $H_{11}C_4N_2CdI_3$ is a polar compound while $H_{12}C_4N_2CdI_4$ is not. Firstly, we believe that the distinct coordination environments of Cd^{2+} ions play a key role. In $H_{12}C_4N_2CdI_4$, the molar ratio of Cd to I is 4, which results in each Cd^{2+} ion being surrounded by only four I atoms, forming a nearly undistorted CdI_4 tetrahedron. In contrast, in $H_{11}C_4N_2CdI_3$, Cd: I is 3, which enables the N atom on the $H_{10}C_4N_2$ unit to participate in Cd^{2+} coordination, forming a distorted CdI_4 and $CdNI_3$ units are 3.27 and 5.94 *D* (Table S10†), respectively, indicating that $CdNI_3$ exhibits more anisotropy, favoring the formation of a polar structure. Finally, the arrangement of Cd^{2+} -centered tetrahedra can also affect the polarity. In $H_{12}C_4N_2CdI_4$, each $H_{12}C_4N_2^{2+}$ cation is surrounded by four CdI₄ tetrahedra, and their dipole moments cancel out each other along the *a*, *b*, and *c* axes (Table S10†). As a result, although $H_{12}C_4N_2CdI_4$ has a noncentrosymmetric structure, it is nonpolar, and its net dipole moment in a unit cell is zero. However, in $H_{11}C_4N_2CdI_3$, the dipole moments of CdNI₃ tetrahedra cancel out each other only along the *b* axis, while they add up along the *a* and *c* axes, resulting in a large net dipole moment of about 17.09 *D* (Table S10†). Therefore, $H_{11}C_4N_2CdI_3$ is a noncentrosymmetric and polar compound.

Thermal and optical properties

Thermogravimetric analysis (TGA) shows the good thermal stabilities of H₁₂C₄N₂CdI₄ and H₁₁C₄N₂CdI₃, at around 300 °C (Fig. 3a). These values are higher than those of previously reorganic-inorganic ported NLO halides. including (H₇C₃N₆)(H₆C₃N₆)HgCl₃ (225 °C),¹⁶ (CH₃NH₃)GeBr₃ (500 K),³⁰ [C₁₈H₂₁N₄][AgI₃]I (260 °C)¹⁸ and Rb₂[PbI₂(HCOO)₂] (240 °C).⁶⁴ The UV-vis spectra show the absorption edges of 291 and 289 nm for H₁₂C₄N₂CdI₄ and H₁₁C₄N₂CdI₃, respectively (Fig. S4[†]). Furthermore, compared to H₁₂C₄N₂CdI₄, H₁₁C₄N₂CdI₃ exhibits a slightly larger bandgap (4.10 eV vs. 3.86 eV) (Fig. 3b), which can primarily be attributed to a reduction in the number of I⁻ ions. Besides, the bandgaps of H₁₂C₄N₂CdI₄ and $H_{11}C_4N_2CdI_3$ are wider than that of the NLO *o*-containing SCALP cation, such as (C₄H₁₀NO)PbCl₃ (3.55 eV),⁶⁵ (C₇H₁₅NCl) $SbCl_4$ (3.05 eV),⁶⁶ (C₆H₅(CH₂)₄NH₃)₄BiI₇·H₂O (2.29 eV),⁴¹ $Rb_2[PbI_2(HCOO)_2]$ (240 °C) (3.40 eV),⁶⁴, (R/S-C₁₆H₂₂N₂Cl)₂· SnCl₆ (3.39 eV)⁶⁷ and (CH₃NH₃)GeBr₃ (2.91 eV).³⁰

SHG properties

Since both $H_{12}C_4N_2CdI_4$ and $H_{11}C_4N_2CdI_3$ are centrosymmetric, their SHG effects are measured according to the method of Kurtz and Perry.⁵⁵ For H₁₂C₄N₂CdI₄, as shown in Fig. S5,[†] the measurement result reveals unwanted non-phase matchable NLO properties, in which the SHG intensity of the crystalline samples exhibits an initial increase, followed by a subsequent decrease as the particle size increased. The maximum value, which is approximately 90 µm, is observed to be about 0.5 times that of KH₂PO₄ (KDP). This phenomenon is reminiscent of the behavior exhibited by traditional phosphate and sulfate compounds, where the CdI₄ tetrahedron exhibits minimal distortion, and its optical anisotropy is mutually canceled within the P212121 space group. Conversely, as shown in Fig. 3c and d, the SHG intensity gradually increased and saturated with increasing particle size, indicating that H₁₁C₄N₂CdI₃ exhibits phase-matching NLO properties. The SHG effect of H₁₁C₄N₂CdI₃ is about six times that of KDP, measured at a particle size of 150-210 µm.

It is interesting to investigate the structure–property relationship among the title compounds and formerly reported Cdcentered NLO OIMHs, such as $[(CH_3)_3NCH_2Cl]CdCl_3$,⁴⁶ $(H_{10}C_4-NO)_2Cd_2Cl_6$,⁴² $(L/D-Hpro)_2Cd_5Cl_{12}$,⁴³ $(L/D-Hpro)(L-pro)CdCl_3$,⁴³ and $L/D-C_{12}H_{20}N_6O_4Cd_2Cl_5$.⁴⁴ The structure of $[(CH_3)_3NCH_2Cl]CdCl_3$ contains a 0D CdCl₆ octahedron, whereas in $(L/D-Hpro)_2Cd_5Cl_{12}$ and $(L/D-Hpro)(L-pro)CdCl_3$, the CdCl₆ octahedra are interconnected into the 2D Cd₅Cl₁₂ layer *via* edge-sharing and the 1D CdCl₃ chain *via* face-sharing, respectively. Notably, such CdCl₆ octahedra only exhibit low optical anisotropy, with very small dipole moments (<0.1 *D*). Hence, their SHG response is relatively weak (<1.0 × KDP). Besides, the N/O atoms in non- π -



Fig. 3 TGA curves (a), UV-vis diffuse reflectance spectra (inset picture is the crystal photo) (b), measured oscilloscope traces of the SHG signals (150–210 mm) (c) and SHG intensity vs. particle size of compounds under 1064 nm laser radiation (d). KDP served as the reference.

conjugated organic groups are sp³ hybridized, which makes them more likely to form coordination bonds with Cd²⁺ cations in non- π -conjugated OIMHs. Therefore, many of them feature an O/Nhybridized polyhedron. In (H₁₀C₄NO)₂Cd₂Cl₆, neighbouring CdCl₆ and CdCl₄O₂ octahedra are bridged into a 1D chain via edge-sharing. L/D-C12H20N6O4Cd2Cl5 contains a CdOCl4 trigonal bipyramid, and each pair of them is formed into a Cd₂O₂Cl₆ dimer via edge-sharing. Importantly, these Cd-O-Cl polyhedra feature larger dipole moments (1.14–5.03 D) that a CdCl₆ octahedron. However, for example, the undesired arrangement of $CdOCl_4$ groups leads to a small net dipole moment (1.19–1.20 D) and weak SHG response in L/D-C₁₂H₂₀N₆O₄Cd₂Cl₅ (~0.2 × KDP). Most importantly, in this work, H₁₂C₄N₂CdI₄ and H₁₁C₄N₂CdI₃ involve CdI₄ (3.27 D) and CdNI₃ (5.94 D) tetrahedra, respectively, in which the polarization magnitudes of CdNI₃ tetrahedra are mutually superimposed along the a- and c-axes resulting in a large net dipole moment of H₁₁C₄N₂CdI₃ (17.09 D) (Table S10⁺). Accordingly, compared with previously reported Cd-centered OIMHs and H₁₂C₄N₂CdI₄, H₁₁C₄N₂CdI₃ features a far large SHG response ($6 \times \text{KDP}$).

Besides, importantly, compared with recently reported NLO OIMHs with SCALP or other d¹⁰-TM cations such as $(C_4H_{10}NO)$ PbBr₃ (0.81 × KDP),⁶⁵ $[C(NH_2)_3]SbF_4$ (2 × KDP),³² $[N(CH_3)_4]$ HgBrI₂ (4.5 × KDP),⁶⁸ (H₇C₃N₆)(H₆C₃N₆)HgCl₃ (5.8 × KDP),¹⁶ α -(CN₃H₆)₃Cu₂I₅ (1.8 × KDP),¹⁹ (CH₃NH₃)GeBr₃ (5.3 × KDP)³⁰ and (C₂₀H₂₀P)CuCl₂ (1.1 × KDP),⁶⁹ H₁₁C₄N₂CdI₃ has a stronger SHG response (6 × KDP). Furthermore, the SHG responses and bandgaps of selected organic–inorganic halides are summarized in Fig. 4 and Table S11† (the relevant references are provided in the ESI†). Unlike other NLO crystals, H₁₁C₄N₂CdI₃ simultaneously exhibits both a strong SHG effect (>5 × KDP) and wide bandgap (>4.0 eV), which makes it promising as a high-performance ultraviolet NLO crystal.

Structure-property relationship analysis

The calculated bandgaps of $H_{12}C_4N_2CdI_4$ and $H_{11}C_4N_2CdI_3$ are provided in Fig. S6,† indicating that they are direct bandgap



organic–inorganic halides. Red ball: compound containing both a π conjugated organic group and SCALP cation, red triangle: compound containing a π -conjugated organic group but without a SCALP cation, blue ball: compound without a π -conjugated organic group but with a SCALP cation, blue triangle: other compounds.

compounds with values of 3.895 and 4.102 eV for $H_{12}C_4N_2CdI_4$ and $H_{11}C_4N_2CdI_3$, respectively, being comparable to the results from measurement (3.86 and 4.10 eV). Partial density of states (PDOS) of $H_{12}C_4N_2CdI_4$ and $H_{11}C_4N_2CdI_3$ is presented in Fig. 5a and b, respectively. The PDOS plots of both compounds are similar. The contribution to the valence band maximum (VBM) mainly comes from the I-p orbitals, as well as a small portion of the Cd-p orbitals. For the conduction band minimum (CBM), the contribution sizes rank in the order of Cd-s, I-p, and I-s orbitals. It is worth noting that in $H_{11}C_4N_2CdI_3$, a small amount of N-p orbitals also contributes to the VBM, which is consistent with the existence of the Cd–N bond. Therefore, we believe that the bandgaps of $H_{12}C_4N_2CdI_4$ and $H_{11}C_4N_2CdI_3$ are determined by the Cd-centered tetrahedra.

Herein, we use the calculated birefringence (Δn) and phase matching wavelength based on the relations between the wavelength and refractive index under both fundamental and harmonic conditions (Fig. 6). Both of them are biaxial crystals with three principal optical axes, *i.e.*, *X*, *Y*, and *Z*. For the orthorhombic crystal H₁₂C₄N₂CdI₄, the calculated refractive index curves after structure optimization show the order of $n_c > n_a > n_b$ in the low-frequency range, and to satisfy the biaxial condition n_X > $n_Y > n_Z$, the transformation of $c \rightarrow x$, $a \rightarrow y$, and $b \rightarrow z$ is performed and a correct order of $n_X > n_Y > n_Z$ is shown in Fig. 6a. For the monoclinic crystal H11C4N2CdI3, the crystallographic axes and principal dielectric axes are not consistent with each other in the ac plane, so the principal dielectric axes in the ac plane must be determined after structure optimization and before the optical calculation. According to the principal axis transformation method in our previous work, the rotation angle θ between the



Fig. 5 The density of states of $H_{12}C_4N_2CdI_4$ and $H_{11}C_4N_2CdI_3$ (b).



Fig. 6 Refractive index dispersion curves for fundamental and second-harmonic light of $H_{12}C_4N_2CdI_4$ (a) and $H_{11}C_4N_2CdI_3$ (b), as well as the calculated birefringence (c). The type-I phase matching wavelengths in different planes were evaluated based on the calculated refractive index, in which we consider the type-I phase matching condition of $n(\omega) = n(2\omega)$.

original coordinate axes (*i.e.* y||b, z||c) and the principal dielectric axes is found to be 25.179°.⁷⁰ After the principal axis transformation and based on the principal dielectric coordinate system, the calculated refractive index curves show an order of $n_X > n_Y > n_Z$ and satisfy the biaxial condition. The shortest wavelengths for type-I phase matching are approximately 592 nm and 466 nm for H₁₂C₄N₂CdI₄ and H₁₁C₄N₂CdI₃, respectively. This implies that under 1064 nm laser radiation, H₁₁C₄N₂CdI₃ can achieve type-I phase matching, while H₁₂C₄N₂CdI₄ cannot. These findings are consistent with our SHG measurements. These calculated birefringences have been obtained from the refractive index difference ($n_X - n_Z$) (Fig. 6c), in which H₁₁C₄N₂CdI₃ possesses a larger birefringence of (0.090 @546 nm, 0.074 @1064

nm) than that of $H_{12}C_4N_2CdI_4$ (0.052 @546 nm, 0.047 @1064 nm). Since piperazine is a non- π conjugated group with negligible contribution of birefringence, the larger birefringence of $H_{11}C_4N_2CdI_3$ can be attributed to the microscopic asymmetry and well-arranged structure of the CdNI₃ group, exemplified by the dipole moment calculation (Table S10†). Consequently, from $H_{12}C_4N_2CdI_4$ to $H_{11}C_4N_2CdI_3$, the polarizable CdNI₃ tetrahedron induces an enlarged birefringence, ensuring phase-matching performance of $H_{11}C_4N_2CdI_3$.

We further calculate the theoretical SHG coefficients of H₁₂C₄N₂CdI₄ and H₁₁C₄N₂CdI₃, as shown in Table S12.[†] For H₁₂C₄N₂CdI₄, it has three non-zero independent SHG tensors with the same value of 0.12 pm V^{-1} , which is about 0.3 times that of KDP (0.39 pm V^{-1}), being consistent with the experimental value (0.5 \times KDP). More importantly, for H₁₁C₄N₂CdI₃, its largest independent SHG tensor is $d_{11} = 2.74 \text{ pm V}^{-1}$, about 7 times larger than that of KDP, which is agreement with the experimental result (6 \times KDP). To explore the origin of the better SHG effect of H₁₁C₄N₂CdI₃, we further calculated the SHG density distribution of the d_{11} tensor (Fig. 7). In the VB, the main source of the SHG effect is the I-5p states. In addition, there are small contributions from the Cd 5s states and the N-2p states from the Cd-N bond. The maximum source in the CB is the Cd-5s orbitals, followed by the I-5s orbitals and the N-2p orbitals in the Cd-N bond. Furthermore, the contributions of each unit to the SHG response are calculated, and the CdNI₃ tetrahedron has a contribution as high as 97.96%. Therefore, we believe that the distorted CdNI₃ tetrahedron is the primary origin of the outstanding SHG effect of $H_{11}C_4N_2CdI_3$.



Fig. 7 SHG density plots for $H_{11}C_4N_2CdI_3$: VB (a) and CB (b).

Conclusions

In summary, we have discovered two new organic-inorganic metal halides (OIMHs), H12C4N2CdI4 and H11C4N2CdI3, by combining the protonated pyrazine cation with d¹⁰-TM-halide tetrahedra. The NLO properties of non- π -conjugated piperazine compounds are studied for the first time. Despite being a noncentrosymmetric compound, H₁₂C₄N₂CdI₄ exhibits a weak and non-phase-matchable SHG effect. In contrast, H11C4N2CdI3 is a polar compound with excellent NLO performance, including a strong SHG response (6 \times KDP), a wide bandgap (4.10 eV), large birefringence (0.074 (a)1064 nm) for phasematching requirement, good thermal stability (300 °C), and a suitable crystal growth habit. The structure-property relationship analysis indicates that the highly polarizable Nhybridized CdNI₃ tetrahedron in the H₁₁C₄N₂CdI₃ structure is the primary cause of the birefringence and SHG effect. Our work provides new insights for exploring semi-organic NLO crystals that do not contain π -conjugated organic components. Further exploration of OIMHs containing N- or O-hybridized metalhalide polyhedra is currently underway.

Data availability

The experimental or computational data can be obtained *via* contacting the corresponding author.

Author contributions

Wu Huai-Yu: conceptualization, methodology, writing – original draft, data curation, visualization; Xu Miao-Bin, Chen Qian-Qian, and Ma Nan: data curation; Hu Chun-Li: formal analysis; Huang Xiao-Ying, Du Ke-Zhao and Chen Jin: writing – review & editing, supervision.

Conflicts of interest

There are no conflicts to declare.

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