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A nickel(II)-based one-dimensional organic–inorganic halide perovskite ferroelectric with the highest Curie temperature†

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Organic–inorganic halide perovskites (OIHPs) are very eye-catching due to their chemical tunability and rich physical properties such as ferroelectricity, magnetism, photovoltaic properties and photoluminescence. However, no nickel-based OIHP ferroelectrics have been reported so far. Here, we designed an ABX₃ OIHP ferroelectric (3-pyrrolinium)NiCl₃, where the 3-pyrrolinium cations are located on the voids surrounded by one-dimensional chains composed of NiCl₆-face-sharing octahedra *via* hydrogen bonding interactions. Such a unique structure enables the (3-pyrrolinium)NiCl₃ with a high spontaneous polarization (P_s) of 5.8 $\mu\text{C cm}^{-2}$ and a high Curie temperature (T_c) of 428 K, realizing dramatic enhancement of 112 and 52 K compared to its isostructural (3-pyrrolinium)MCl₃ (M = Cd, Mn). To our knowledge, remarkably, (3-pyrrolinium)NiCl₃ should be the first case of nickel(II)-based OIHP ferroelectric to date, and its T_c of 428 K (35 K above that of BaTiO₃) is the highest among all reported one-dimensional OIHP ferroelectrics. This work offers a new structural building block for enriching the family of OIHP structures and will inspire the further exploration of new nickel(II)-based OIHP ferroelectrics.

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Introduction

Organic–inorganic halide perovskites (OIHPs) have caught phenomenal research attention in recent years for their promising application potential in photovoltaics,¹ photoelectricity,^{2,3} light emitting diodes,⁴ ferroelectric memory,^{5,6} and electron spin devices.^{7,8} Among them, ferroelectrics feature switchable spontaneous polarization that acts as the essential core in nonvolatile memory, capacitors and sensors, *etc.*^{9–14} OIHPs have occupied an important position in the ferroelectric field by taking advantage of their chemical tunability, light weight, mechanical flexibility and so on, compared with their inorganic counterparts. Structurally, OIHPs with the typical ABX₃-type (A = organic cation, B = metal cation, and X = halide anion) formula generally adopt two structural forms, either a three-dimensional BX₆-corner-sharing cubic structure or a one-dimensional BX₆-face-sharing hexagonal structure.^{15–17} The A-site organic cations are embedded in the voids surrounded by the inorganic framework of BX₆

octahedra *via* weak interactions, endowing the OIHPs with great structural diversity and chemical variability.^{18–23} Such unique structural characteristics open a rich platform for design synthesis and performance optimization of ferroelectric materials.^{24–33} Nevertheless, hundreds of ABX₃-type OIHPs have been discovered, while only a few cases show ferroelectricity. Exploring reliable design concepts to assemble OIHP structures for developing high-performance ferroelectrics is an imminent ongoing challenge.

To be a ferroelectric, the crystal must have polar symmetry, whose polarization switching is inseparable from the reorientational arrangement of molecular dipoles in lattice. Accordingly, several design strategies involving chemical modifications on organic cations of OIHPs have been proposed to efficiently obtain molecular ferroelectrics.^{34–36} For example, by modifying some structurally flexible building blocks, like spherical [(CH₃)₄N]⁺, 1,4-diazabicyclo[2.2.2]octonium (Dabco) and quinuclidine, to be suitable A-site cations, a series of OIHP ferroelectrics have been designed with superior performance such as multiple polarization axes, large piezoelectric response and high Curie temperature (T_c).^{37–45} Emphatically, a high T_c is essential for ferroelectric applications because it directly determines the working temperature range in many areas. Besides the organic cation itself, the weak interactions between organic and inorganic components in OIHPs cannot be ignored, which play an important role in crystallographic engineering to induce desired physical properties.^{46–49} Previous studies have demonstrated the rational modifications on A-site organic cations to modulate weak interactions to realize the design and performance optimization of

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OIHP ferroelectrics such as (4,4-difluorohexahydroazepine)₂PbI₄,³⁷ and (ethylammonium)₂(EA)₂Pb₃Br₁₀.⁵⁰ In this stage, it has to be mentioned that, however, the BX₆ inorganic components in OIHPs are equally important while they are always easily overlooked under the halo of organic components. BX₆ octahedra in the reported ferroelectric OIHPs also have considerable diversity, with a variety of optional B-site metal ions such as Pb²⁺, Mn²⁺, Cd²⁺, Cr²⁺, Sn²⁺ and so on.^{51–58} Notably, Xiong *et al.* reported a special nickel(II) nitrite-based organic–inorganic hybrid perovskite ferroelectric, [N-fluoromethyl tropine][Ni(NO₂)₃], designed by rational chemical modification and structural assembly.⁵⁹ Zhang *et al.* also reported several zero-dimensional packing phase transition materials with the Ni(NCS)₆ framework.⁶⁰ For nickel(II) halide crystals, a series of perovskite variants ABX₃ (B = Ni, A = Gu, FA, MA, X = Cl, Br; B = Mn, A = MA, X = Br) have been demonstrated to show optical properties and high electronic capacity (CH₃NH₃-NiCl₃).^{61,62} However, no nickel(II) halide-based OIHP ferroelectrics have been reported so far.

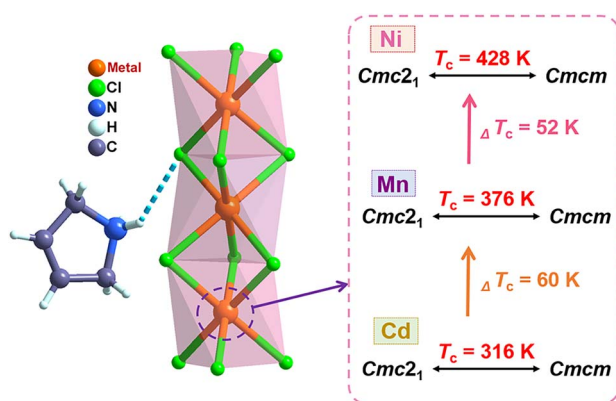
In the OIHP system, particularly, the 3-pyrrolinium cation has been shown to be a very promising candidate and an effective functional unit for building ferroelectrics, as reported in several previous studies such as (3-pyrrolinium)CdBr₃ and (3-pyrrolinium)MCl₃ (M = Cd, Mn).^{29,55,56} On the other hand, compared to Mn(II) and Cd(II), the six-coordinated Ni(II) with a smaller radius can form a smaller nickel(II) halide octahedron with a reduced octahedron volume, which may compress the space for organic cation movements and reduce the distance of hydrogen bonding interactions, thereby resulting in high phase transition temperature. Accordingly, through an elaborate structural assembly, we here present a new nickel(II)-based OIHP ferroelectric, (3-pyrrolinium)NiCl₃, with a high T_c of 428 K, above that (about 393 K) of the inorganic perovskite ferroelectric BaTiO₃.⁶³ Systematic characterization reveals its remarkable ferroelectricity with a high saturated polarization (P_s) of 5.8 μC cm⁻², and the order–disorder transition of the 3-pyrrolinium cations which leads to a ferroelectric phase transition. Compared to its isostructural compounds previously reported, (3-pyrrolinium)MCl₃ (M = Cd, Mn) (Scheme 1),^{55,56} the variation of the inorganic framework of BX₆ octahedra enables the T_c to get a significant increase of 112 and 52 K, due to the stronger

hydrogen bonding interactions that act as a rope between the 3-pyrrolinium cations and [NiCl₃]⁻ anionic chains. Moreover, to our knowledge, (3-pyrrolinium)NiCl₃ should be the first case of nickel(II)-based OIHP ferroelectric to date, which could provide a new structural paradigm for one-dimensional ABX₃ OIHP ferroelectrics. More importantly, its T_c of 428 K is the highest among all reported one-dimensional OIHP ferroelectrics, making it competitive for ferroelectric-related devices with a wide operating temperature range.

Results and discussion

(3-Pyrrolinium)NiCl₃ was prepared by the reaction of 3-pyrrolinium chloride and nickel chloride in dilute hydrochloric acid solution, and its prism-like colorless crystals were easily obtained by a slow solution evaporating method. The preliminary differential scanning calorimetry (DSC) traces show a pair of endothermic/exothermic peaks in the heating/cooling runs (Fig. 1), indicating a reversible phase transition at about 428 K (Curie temperature, T_c), higher than those of the analogous (3-pyrrolinium)CdCl₃ (T_c = 316 K) and (3-pyrrolinium)MnCl₃ (T_c = 376 K).

To understand the phase transition mechanism and ferroelectric origin of (3-pyrrolinium)NiCl₃, we determined its crystal structures and the resulting crystal data at various temperatures are summarized in Table S1.† (3-Pyrrolinium)NiCl₃ adopts a one-dimensional hexagonal ABX₃-type perovskite structure, where the infinite linear chains of the face-sharing NiCl₆ octahedron along the [0 0 1] direction are separated by the A-site 3-pyrrolinium cations (Fig. 2). The anion chains and organic cations are loosely connected by N–H⋯Cl hydrogen bonding interactions. At room temperature in the phase below T_c (marked as LTP), the (3-pyrrolinium)NiCl₃ crystallized in an orthorhombic space group *Cmc2*₁ (polar point group *mm2*) with the well-ordered 3-pyrrolinium cations and distorted NiCl₆ octahedra. From the packing view of the crystal structure, all of the 3-pyrrolinium cations are aligned along the *c*-axis, which could result in a spontaneous polarization. On the basis of the point charge model for (3-pyrrolinium)NiCl₃ in LTP (Fig. S1†), the estimated spontaneous polarization along the [0 0 1] direction is about 6.08 μC cm⁻². In the phase above T_c (marked as HTP), the crystal symmetry of (3-pyrrolinium)NiCl₃ transforms into the centrosymmetric space group *Cmcm*, which belongs to the point group *mmm*. Such crystallographic symmetry of *mmm* cancels out the molecular dipoles in each direction, leading to zero macroscopic polarization. In the HTP, the 3-pyrrolinium cations are located on the special symmetry site of *2mm* in the lattice, and



Scheme 1 The design concept of ferroelectric (3-pyrrolinium)NiCl₃ with the one-dimensional ABX₃ OIHP structure.

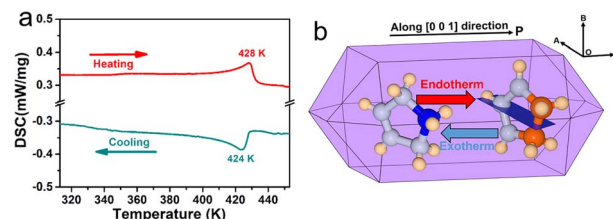


Fig. 1 (a) DSC curves of (3-pyrrolinium)NiCl₃ in heating/cooling runs. (b) Simulative single crystal shape of (3-pyrrolinium)NiCl₃.



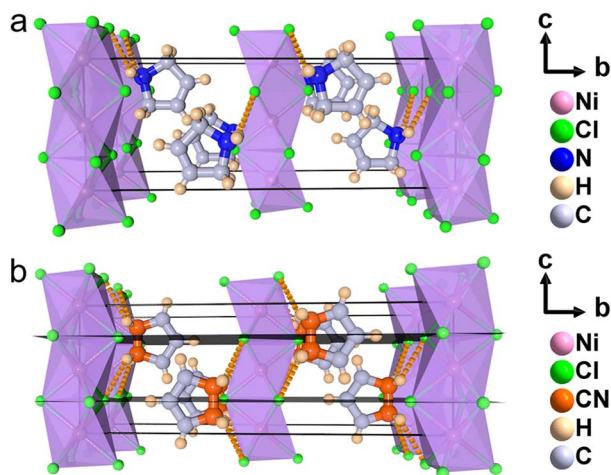


Fig. 2 Packing view of crystal structures of (3-pyrrolinium)NiCl₃ in (a) LTP and (b) HTP. The orange dotted lines represent N–H...Cl hydrogen bonding, and the black plane represents mirror symmetry elements.

consequently the cations are required to show 2-fold orientational disorder, where the C and N atoms distribute equally in two positions by the mirror plane symmetry perpendicular to the *c*-axis. The anion chains of the NiCl₆ octahedron experience little change except the octahedron become more regular. Therefore, the phase transition mechanism can be mainly attributed to the order-disorder transition of 3-pyrrolinium cations. From HTP to LTP, the symmetric elements are halved from eight ($E, i, C_2, 2C_2', \sigma_h, 2\sigma_v$) in HTP to four ($E, C_2, 2\sigma_v$) in LTP (Fig. S2†). The symmetry breaking occurs with the disappearance of the mirror element, leading to the orientational ordering of cations to generate spontaneous polarization, which means that the (3-pyrrolinium)NiCl₃ is an $mmmFmm2$ -type ferroelectric with two equivalent polarization directions.

The stacking structure and phase transition mechanism of (3-pyrrolinium)NiCl₃ are similar to those of (3-pyrrolinium)MCl₃ (M = Cd, Mn), while the T_c has been greatly improved to up to 428 K. This would be closely associated with the changes of hydrogen-bonding interactions by different inorganic anion chains, and then affect the energy barrier of cationic orientational motions. As shown in Fig. 3a–c, for (3-pyrrolinium)MCl₃ (M = Cd, Mn, Ni), the M–Cl bond distances undergo a decrease in sequence from Cd, Mn to Ni, with the range changes from 2.621–2.669 Å to 2.527–2.583 Å to 2.390–2.464 Å. Obviously, the MCl₆ (M = Cd, Mn, Ni) octahedra gradually become smaller with the variable M–M distances in anion chains from 3.341 Å to 3.234 Å to 3.089 Å. The M–M distances between adjacent anion chains also experienced a gradual decrease with the changes of MCl₆ octahedra from Cd, Mn to Ni (Fig. S3†). These changes make the void smaller, resulting in a confinement effect to increase the energy for cation rotation (Table S2†). Based on the Density Functional Theory (DFT) calculations, the energy barrier for the rotation of 3-pyrrolinium cations in (3-pyrrolinium)MCl₃ (M = Cd, Mn, Ni) are 4.27, 4.51, and 4.97 eV respectively (Fig. S4–S7 and Table S3†), which indicates that (3-pyrrolinium)NiCl₃ has a higher T_c , consistent with the results for structural analysis. In the OIHP system, besides the

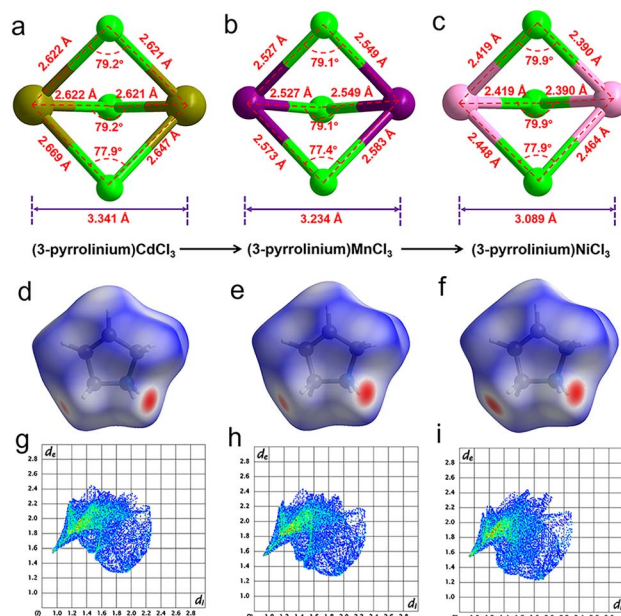


Fig. 3 Comparison of anionic chains of (a) (3-pyrrolinium)CdCl₃, (b) (3-pyrrolinium)MnCl₃ and (c) (3-pyrrolinium)NiCl₃. The Hirshfeld d_{norm} surfaces (d–f) and two-dimensional (2D) fingerprint plots (g–i) for the 3-pyrrolinium cations in (3-pyrrolinium)MCl₃ (M = Cd, Mn, Ni). The d_i of the *x*-axis coordinate and the d_e of the *y*-axis represent the distance (Å) from the atoms inside the cation to the Hirshfeld surface and the external atoms to the Hirshfeld surface respectively.

anionic component, hydrogen bonding interactions also have to be considered, which have been utilized as an indispensable tool in crystal engineering to design desired physical properties. The N–H...Cl hydrogen-bonding in (3-pyrrolinium)NiCl₃ is stronger than the other two compounds, which can be clearly seen from the shortest distance between the donor (N) and acceptor (Cl) in (3-pyrrolinium)MCl₃ (M = Cd, Mn, Ni) with 3.335, 3.306 and 3.302 Å respectively (Fig. S3†). The Hirshfeld d_{norm} surfaces and related 2D fingerprint plots of 3-pyrrolinium cations in (3-pyrrolinium)MCl₃ (M = Cd, Mn, Ni) were further calculated to get the information about the environment of cations and intermolecular contacts (Fig. 3d–i).

From the Hirshfeld d_{norm} surfaces, the short contacts (represented by the deep red circular depressions on the surfaces) between the cation and its surroundings for (3-pyrrolinium)NiCl₃ are closer than those for (3-pyrrolinium)MCl₃ (M = Cd, Mn), which are reflected in 2D fingerprints by quantifying the mean d_{norm} value for (3-pyrrolinium)NiCl₃ (0.384), (3-pyrrolinium)MnCl₃ (0.422) and (3-pyrrolinium)CdCl₃ (0.424). The calculated results show that the total interactions in (3-pyrrolinium)NiCl₃ are stronger than those in (3-pyrrolinium)MCl₃ (M = Cd, Mn), which like a strong rope pull the cations, leading to a larger energy barrier required for the structural phase transition of (3-pyrrolinium)NiCl₃.

Ferroelectric phase transitions are generally accompanied by significant anomalies of dielectric permittivity at around T_c . For (3-pyrrolinium)NiCl₃, the real part ϵ' of the complex dielectric constant exhibits a sharp λ -shaped peak-like response at about $T_c = 428$ K in each frequency (Fig. 4a). The peak values are several



hundred to one thousand times larger than those in the stable state. We also carried out the second harmonic generation (SHG) measurements to study the symmetry changes of (3-pyrrolinium)NiCl₃ during ferroelectric phase transition, by taking advantage of the high sensitivity of the SHG response to the breaking of the space-inversion symmetry. The SHG signal shows non-zero intensity in LTP (ferroelectric phase), consistent with the polar space group *Cmc*2₁, and experiences a change with temperature increasing until *T*_c (Fig. 4b). Above *T*_c, the SHG signal becomes inactive and maintains the zero intensity in HTP (paraelectric phase), corresponding to the centrosymmetric space group *Cmcm*.

The ferroelectricity with polarization reversal of (3-pyrrolinium)NiCl₃ was directly verified by measuring polarization–electric field (*P*–*E*) hysteresis loops (Fig. 5). A linear *P*–*E* curve was obtained at 443 K above its *T*_c, indicating that it is currently in the paraelectric phase. On cooling to 428 K at about *T*_c, the result begins to show a compressed S-shaped curve. And then, the *P*–*E* curve opens to form a typical loop at 423 K below *T*_c, entering the ferroelectric phase. Upon further cooling, the ferroelectric loops expand and the *P*_r (remnant polarization) value increases gradually to reach about 5.8 μC cm⁻² at 303 K, in accordance with the estimated value of 6.08 μC cm⁻² from the crystal structure. The measured saturated polarization (*P*_s) and remnant polarization (*P*_r) values are close to each other. The polarization value of 5.8 μC cm⁻² is higher than those of the ABX₃-type OIHP ferroelectrics reported thus far (Table S4[†]), and larger than that of the reported nickel(II)

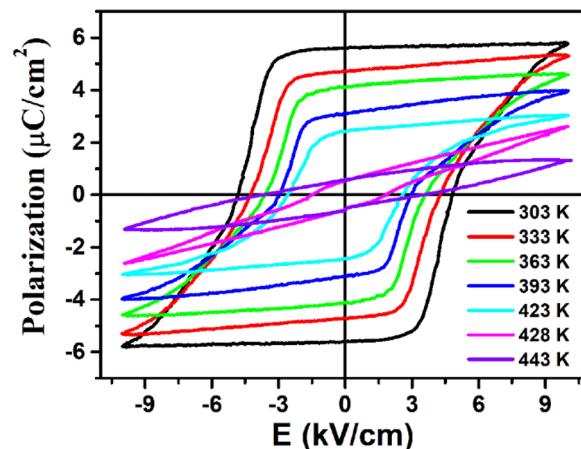


Fig. 5 Ferroelectric hysteresis loops of (3-pyrrolinium)NiCl₃ measured at different temperatures in the LTP.

nitrite-based hybrid perovskite ferroelectric [N-fluoromethyl tropine][Ni(NO₂)₃] (3.0 μC cm⁻²). Moreover, its *T*_c of 428 K should be the highest among all reported one-dimensional OIHP ferroelectrics (Table S4[†]), which combined with the small coercive field *E*_c in the range of 2.6–4.8 kV cm⁻¹, makes (3-pyrrolinium)NiCl₃ more competitive for relatively high-temperature, low operation voltage, low-power information storage devices.

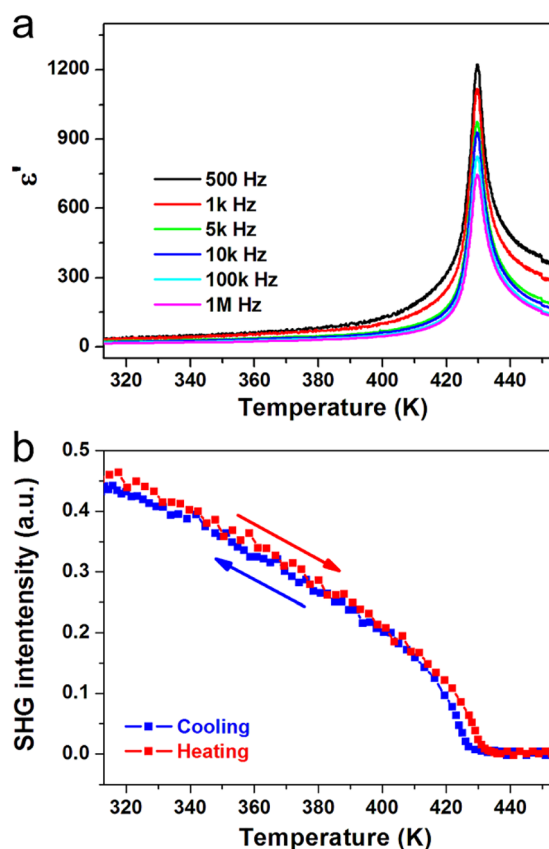


Fig. 4 Temperature-dependent (a) real part of the complex dielectric constant and (b) SHG intensity of (3-pyrrolinium)NiCl₃.

Conclusions

In summary, we successfully designed a new nickel(II)-based OIHP ferroelectric, (3-pyrrolinium)NiCl₃, through an elaborate structural assembly of 3-pyrrolinium organic cations and one-dimensional [NiCl₃]_n⁻ chains of NiCl₆-face-sharing octahedra. It undergoes an *mmmFmm*2-type ferroelectric phase transition at 428 K, induced by the thermally driven transition of 3-pyrrolinium cations. The confined environment of 3-pyrrolinium cations caused by anion chains and relatively strong hydrogen bonding interactions give rise to a high energy barrier for phase transition, inducing ferroelectricity up to a high Curie temperature of 428 K. To our knowledge, such a *T*_c of 428 K should be the highest among all reported one-dimensional OIHP ferroelectrics, offering a wide operating temperature range for ferroelectric-related devices. More strikingly, (3-pyrrolinium)NiCl₃ is the first nickel(II)-based OIHP ferroelectric, enriching the hybrid perovskite ferroelectric families. Considering the structural diversity and chemical tunability of OIHPs, one can expect more such nickel(II)-based OIHPs to be discovered with excellent ferroelectricity.

Author contributions

H.-F. N. conceived the experiments and wrote the paper. L.-K. Y., P.-C. Z. G., B.-L. H. and J.-R. L. performed the experiments. C.-Y. S. and Z.-X. Z. assisted in the auxiliary analysis of data. L.-Y. X., D.-W. F. and Y. Z. guided and supervised this work.



Conflicts of interest

The authors declare no conflict of interest.

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