

## Communication

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# Homochiral Nickel Nitrite ABX<sub>3</sub> (X = NO<sub>2</sub><sup>-</sup>) Perovskite Ferroelectrics

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Supporting Information Placeholder

**ABSTRACT:** Chiral organic-inorganic perovskites (COIPs) have recently attracted increasing interest due to their unique inherent chirality and potential applications in next-generation optoelectronic and spintronic devices. However, COIP ferroelectrics are very sparse. In this paper, for the first time, we present the nickel-nitrite ABX3 COIP ferroelectrics, [R- and S-Nfluoromethyl-3-quinuclidinol]Ni(NO2)3 ([*R*-*S*and FMQ]Ni(NO<sub>2</sub>)<sub>3</sub>), where the X-site is the rarely seen NO<sub>2</sub><sup>-</sup> bridging ligand. [R- and S-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> display mirror-relationship in the crystal structure and the vibrational circular dichroism signal. It is emphasized that [R- and S-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> show splendid ferroelectricity with both an extremely high phase-transition point of 405 K and spontaneous polarization of 12  $\mu$ C/cm<sup>2</sup>. To our knowledge, [R- and S-FMO]Ni(NO<sub>2</sub>)<sub>3</sub> are the first examples of nickel-nitrite based COIP ferroelectrics. This finding expands the COIP family and throws lights on exploring high-performance COIP ferroelectrics.

Perovskites, which have the simplest general ABX<sub>3</sub> (A, B are cations, and X is the anion) formula, represent a large family of important functional materials. Among them, the inorganic oxide perovskites where X-site is the oxygen ion have received great interest for centuries because of their intriguing physical properties and wide practical applications.<sup>1</sup> In recent years, the halide perovskites (X-site = halogen ions) have shown promising applications in optoelectronic devices such as photovoltaics, which aroused significant attention to organic-inorganic perovskites (OIPs).<sup>2</sup> OIPs are structurally derived from the inorganic oxide perovskites, and their structure generally consists of organic Asite cation and inorganic framework of BX6 octahedral.<sup>3</sup> Combining the features of organic and inorganic constituents, OIPs can be easily solution-processed into nanostructures, thin films and crystals, and they show excellent optical, magnetic, and electric properties.<sup>4</sup> For instance, [CH<sub>3</sub>NH<sub>3</sub>]<sup>+</sup> based lead halide OIPs exhibit high photoluminescence efficiency and absorption coefficient.<sup>5</sup>  $[(CH_3)_2NH_2][B(HCOO)_3]$  (B = Mn<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup>, and Co<sup>2+</sup>) were found to show weak ferromagnetism and antiferroelectric order.<sup>6</sup> [ClCH<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>N]CdCl<sub>3</sub> and its solid solution [FCH<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>x</sub>[ClCH<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>N]<sub>1-x</sub>CdCl<sub>3</sub> show larger piezoelectric coefficient than the inorganic perovskite BaTiO3 and Pb(Zr,Ti)O<sub>3</sub>, respectively. <sup>7</sup>

Recently, the incorporation of chiral A-site cation endows OIPs with the unique inherent chirality, which is very hard to be achieved in the inorganic oxide counterparts due to the absence of intrinsic chiral centers.<sup>8</sup> The inherent chirality of chiral (homochiral) organic-inorganic perovskites (COIPs) brings fascinating physical features including circular dichroism, chiroptical nonlinear optical effect, circularly polarized photoluminescence, and spintronic property,<sup>9</sup> showing potential applications in future optical and spintronic devices,10 which makes COIPs particularly appealing. Since five of ten polar point groups for generating ferroelectricity are chiral-polar ( $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$  and  $C_6$ ) and 22 of 88 types of paraelectric-to-ferroelectric phase transition are chiralto-chiral (Table S1),<sup>11</sup> the introduction of chirality into OIPs also facilitates the realization of ferroelectricity, a functional property that plays a vital role in non-volatile memories.<sup>12</sup> Several halide ABX<sub>3</sub> COIP ferroelectrics were recently constructed based on the chiral [R- and S-3-fluoro-pyrrolidinium]<sup>+</sup> cation.<sup>13</sup> However, they suffer from a low phase-transition temperature ( $T_c$ , 273-333 K) and small spontaneous polarization ( $P_s$ , 4.5-5.79  $\mu$ C/cm<sup>2</sup>),<sup>13</sup> significantly smaller than those (393 K and 26  $\mu$ C/cm<sup>2</sup>) of the oxide perovskite ferroelectric BaTiO<sub>3</sub>,<sup>14</sup> which hinders their further applications. Most recently, Shi and coworkers reported the lead halide ABX<sub>3</sub> COIP ferroelectrics [*R*and Scyclohexylethylammonium]PbI<sub>3</sub> with  $T_c$  of 373 K, but the  $P_s$  is only 1.2  $\mu$ C/cm<sup>2.15</sup> Although many OIP ferroelectrics have been discovered,<sup>16</sup> the COIP ferroelectrics remain very few, especially for the both high  $T_c$  and high  $P_s$  ones.

Owing to the structural flexibility of OIPs, beyond the most commonly seen halogen ions, the X-site ions can be extended to other bridging ligands such as the formate ([HCOO]<sup>-</sup>), hypophosphite ([H<sub>2</sub>POO]<sup>-</sup>), cyanide (CN<sup>-</sup>), thiocyanate (SCN<sup>-</sup>), dicyanamide ([N(CN)<sub>2</sub>]<sup>-</sup>), perchlorate (ClO<sub>4</sub><sup>-</sup>), tetrafluoroborate (BF<sub>4</sub><sup>-</sup>), and nitrate (NO<sub>3</sub><sup>-</sup>) ions.<sup>4a,17</sup> However, the COIP ferroelectrics are mainly found in the halide OIPs.4a,17 Herein, we reported unprecedented nickel-nitrite COIP ferroelectrics [R- and S-Nfluoromethyl-3-quinuclidinol]Ni(NO<sub>2</sub>)<sub>3</sub> and ([*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub>), where the X-site is the  $NO_2^-$  ion. They show mirror-related vibrational circular dichroism (VCD) response. More importantly, the T<sub>c</sub> and P<sub>s</sub> of [R-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [S-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> reach up to 405 K and 12  $\mu$ C/cm<sup>2</sup>, respectively, which greatly exceeds those of recently documented halide ABX3 COIP ferroelectrics, <sup>13,15</sup> and is one of the highest value in molecular ferroelectrics.<sup>13-16,18</sup> [R-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [S-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> are the first nickel-nitrite COIP ferroelectrics, which broadens the class of COIPs and provides promising platforms for achieving excellent COIP ferroelectrics.

Single-crystal structural measurements reveal that [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> have the identical monoclinic chiral-polar *P*2<sub>1</sub> crystal symmetry with *C*<sub>2</sub> point group in the ferroelectric phase (FP) at 293 K (Table S2). [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> has the typical hexagonal ABX<sub>3</sub> perovskite structure (Figure 1a),<sup>13</sup> where the A, B, and X represents the [*R*-FMQ]<sup>+</sup>, Ni<sup>2+</sup>, and NO<sub>2</sub><sup>-</sup> ions, respectively, and the [*R*-FMQ]<sup>+</sup> cations



Figure 1. Crystal structure of (a) [R-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and (b) [S-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> at 293 K viewed along the a-axis.

reside in the space between adjacent one-dimensional  $(Ni(NO_2)_3)_n^-$  anionic chains of face-sharing  $Ni(NO_2)_6$  octahedral. In the  $Ni(NO_2)_6$  octahedron, the center Ni atom is surrounded by 3 N and 3 O atoms from  $6 NO_2^-$  ligands with the Ni–N and Ni–O distances in the range of 2.060(7)-2.098(7)Å and 2.053(6)-2.061(7)Å, respectively (Table S3). Such octahedron thus has the O–Ni–N angles (83.5(2)-176.7(3) °), N–Ni–N angles (91.1(3)-94.9(3) °), and O–Ni–O angles (94.0(3)-97.9(2) °) (Table S3), implying a significant distortion. The [*R*-FMQ]<sup>+</sup> cation is ordered, which has a chiral center with the "*R*" configuration (Figure 1a). Structurally, [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> (Figure 1a and b).

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VCD is a spectral technology widely applied to identify the chiral properties of the enantiomers. Figure 2a shows the VCD spectra of [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub>, displaying several couples of obvious signals at around 1376, 1363, 1350, 1330 and 1312 cm<sup>-1</sup>. These VCD signals are consistent with the absorption peaks observed in the infrared spectra (Figure 2b). Their infrared spectra match well with each other. Whereas, the VCD spectra almost present a mirror image. This demonstrates the enantiomeric characteristics of [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> crystals. We also calculated the VCD and infrared spectra of [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> by densityfunctional theory (Figure 2c). The obtained VCD signal show mirror-relationship as well. There is a minor peak shift between the experimental and calculated spectra because of the molecular configuration variation when optimizing the geometry.

We then adopted DSC (differential scanning calorimetry) analyses for [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> to trace the phase transition. Their DSC curves present reversible anomaly peaks in the heating-cooling process (Figure 3a and b), reflecting the presence of phase transition. The  $T_c$  deduced from the peak position of the heating curve is 405 K for the enantiomers. This value exceeds the  $T_c$  of the majority of OIP ferroelectrics, such as the chiral halide perovskite [*R*-3-fluoro-pyrrolidinium]MnBr<sub>3</sub> (273 K),<sup>13a</sup> the lead halide perovskite [ICH<sub>2</sub>N(Me)<sub>3</sub>]PbI<sub>3</sub> (312 K),<sup>16d</sup> the metal-formate perovskite [(N<sub>2</sub>H<sub>5</sub>)<sub>x</sub>(CH<sub>3</sub>NH<sub>3</sub>)<sub>1-</sub> x]Mn(HCOO)<sub>3</sub> (287 K–355 K),<sup>16f</sup> and also surpasses the  $T_c$  of the inorganic oxide perovskite BaTiO<sub>3</sub> (393 K).<sup>14</sup> The high  $T_c$  feature ensures [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> could work at a wide temperature range.

We further collected the crystal data of [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> at 423 K above *T*<sub>c</sub> in the paraelectric phase (PP), the obtained cell parameters indicate a trigonal or hexagonal crystal system with *a* = 10.7360 Å, *b* = 10.7360 Å, *c* = 6.8249 Å,  $\alpha = \beta = 90^{\circ}$ , and  $\gamma = 120^{\circ}$  for [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and *a* = 10.7093 Å, *b* = 10.7093 Å, *c* = 6.8345 Å,  $\alpha = \beta = 90^{\circ}$ , and  $\gamma = 120^{\circ}$  for [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub>. However, the crystal data are poor, and it is hard to solve the crystal structure well. We also recorded the powder X-ray diffraction (XRD) data at various temperatures for [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> (Figure S1). The XRD



**Figure 2.** (a,b) Measured and (c) calculated VCD and infrared (IR) spectra of [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub>.

peaks at 293 K are consistent with those obtained by the crystal structural simulation. They experience no apparent variation with temperature rising in FP. Nevertheless, when the temperature goes up to the PP, the XRD peak number lessens obviously, which means a higher crystal symmetry.

The phase transition course is normally along with the dielectric anomaly. As expected, the real part  $\varepsilon'$  of dielectric constant versus temperature for [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> displays an abruptly jump as the temperature increases near *T*<sub>c</sub>. Generally, the ferroelectric-to-paraelectric phase transitions obey Curie-Weiss law:

#### $X = C/(T - T_c)$

in which *X*, *C*, *T*, and *T*<sub>c</sub> represents the electrical susceptibility, a constant, an absolute temperature and the Curie temperature, respectively. However, in our case, the  $\varepsilon'$  shows a step-fashion curve rather than a typical  $\lambda$  peak shape of the dielectric anomaly for ordinary proper ferroelectrics based on the Curie-Weiss law. This manifests that [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> are improper ferroelectric, where the  $\varepsilon'$  does not follow the Curie-Weiss law. We thus used a model based on the Landau-Ginzburg theory (supporting information), which is applicable to describe dielectric behaviors of improper ferroelectrics,<sup>7a</sup> to fit the  $\varepsilon'$  versus temperature curve. The obtained fitting curves match well with the measured ones in the FP region (Figure 3c and d), but not very well in the PP region, as observed in the improper ferroelectric

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[ClCH<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>N]MnCl<sub>3</sub>.<sup>7a</sup> This is due to that for realistic improper ferroelectrics, the measured dielectric constants in PP are always temperature-dependent while not the theoretically temperatureindependent (see supporting information).<sup>7a,16e</sup> The ε' of [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> exhibits an enhancement in PP, as found in other improper ferroelectrics like [(OH)N(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>KFe(CN)<sub>6</sub>,<sup>16e</sup> which may be attributed to the significantly disordered dipolar organic cations in PP (see below).

As is generally known, solid materials crystallizing in the noncentrosymmetric point groups (except for  $D_4$ ,  $D_6$ , and O based on Kleinman's symmetry transformation<sup>19</sup>) are SHG (second harmonic generation) responsive. Both [R-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [S-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> (Figures 4a and b) are SHG-responsive in FP, which corresponds to the chiral-polar  $C_2$  point group. When the temperature is raised, the SHG signals drop to background value at around  $T_{\rm c}$ . Thus, in view of the chirality and the trigonal or hexagonal crystal system, the PP of [R-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [S-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> may take the SHG-unresponsive chiral-nonpolar  $D_6$  point group. In this high symmetry phase, the [*R*-FMQ]<sup>+</sup> and [S-FMQ]<sup>+</sup> cations will become significantly disordered, of which the order-disorder transition contributes to the phase transition, as found in other OIP ferroelectrics.<sup>7,13,16</sup> The large  $[R-FMO]^+$  and [S-FMQ]<sup>+</sup> cations need a large energy barrier to accomplish the order-disorder transition, being responsible for the high  $T_{\rm c}$ .<sup>11b</sup>

The ferroelectricity of [R-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [S-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> is directly ascertained by characterizing the P-E(polarization-electric field) loop. Figure 4c and d reveal a clear P-E loop, which is the crucial evidence for ferroelectricity. The Ps at 293 K of [R-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [S-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> equals to 12  $\mu$ C/cm<sup>2</sup>, which is one of the largest value in molecular ferroelectric  $^{13-16,18}$  This value also surpasses the  $P_{\rm s}$  of the recently documented halide ABX<sub>3</sub> COIP ferroelectrics (1.2-5.79  $\mu C/cm^2),^{13,15}$  and other OIP ferroelectrics including the halide  $\mu$ C/cm<sup>2</sup>),<sup>16b</sup>  $(C_5H_{12}NO)_2PbBr_4$ (5.6 the cyanide  $[(OH)N(CH_3)_3]_2KFe(CN)_6$  (1.25  $\mu$ C/cm<sup>2</sup>),<sup>16e</sup> and the formate  $(N_2H_5)Mn(HCOO)_3$  (3.58 µC/cm<sup>2</sup>).<sup>20</sup> Structurally, the alignment of dipole moments of the NO<sub>2</sub><sup>-</sup> ions within the  $(Ni(NO_2)_3)_n$  chain of distorted Ni(NO<sub>2</sub>)<sub>6</sub> octahedral and the [R- and  $S-FMO]^+$  cations contributes to the large Ps of [R-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [S-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub>. To further estimate the saturated polarization, the point charge model is employed for calculation (supporting information). The calculated  $P_s$  is in line with the measured value.

We also synthesized other nickel-nitrite COIPs, [*R*- and *S*-*N*-methyl-3-quinuclidinol]Ni(NO<sub>2</sub>)<sub>3</sub> ([*R*- and *S*-MQ]Ni(NO<sub>2</sub>)<sub>3</sub>), which are structurally analogous to [*R*- and *S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub>, respectively (Figure S2). [*R*- and *S*-MQ]Ni(NO<sub>2</sub>)<sub>3</sub> adopt chiral-polar *P*2<sub>1</sub> crystal symmetry in FP as well, and own a high *T*<sub>c</sub> reaching 372 K and high *P*<sub>s</sub> reaching 11.7  $\mu$ C/cm<sup>2</sup> (Table S2, and Figures S2-S6). [*R*- and *S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> have a higher *T*<sub>c</sub> than [*R*- and *S*-MQ]Ni(NO<sub>2</sub>)<sub>3</sub> because of the larger fluorinated [*R*- and *S*-FMQ]<sup>+</sup> cations.

In summary, we reported the first nickel-nitrite ABX<sub>3</sub> COIP ferroelectrics. They have the typical hexagonal ABX<sub>3</sub> structure with the NO<sub>2</sub><sup>-</sup> ion as the X-site and show VCD response. Intriguingly, [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> possess both an exceptionally high  $T_c$  reaching up to 405 K and high  $P_s$  reaching up to 12  $\mu$ C/cm<sup>2</sup>, which is outstanding in OIPs, and significantly surpasses those of the recently documented halide ABX<sub>3</sub> COIP ferroelectrics. We anticipate that by incorporating more chiral organic A-site cations into nickel-nitrite OIPs, more new splendid COIPs can be assembled.



**Figure 3.** (a,b) DSC results and (c,d) variable-temperature  $\varepsilon'$  upon heating for [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub>.



Figure 4. (a,b) SHG response versus temperature and (c,d) P-E loop obtained at 293 K for [*R*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub> and [*S*-FMQ]Ni(NO<sub>2</sub>)<sub>3</sub>.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, Figures S1–S6, Tables S1–S3, model for fitting temperature-dependent  $\varepsilon'$ , calculation of polarization, and X-ray crystallographic data.

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#### Notes

The authors declare no competing financial interest.

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### REFERENCES

(1) Tejuca, L. G.; Fierro, J. L. Properties and Applications of Perovskite-Type Oxides; CRC Press: New York, 1993.

(2) (a) Jena, A. K.; Kulkarni, A.; Miyasaka, T. Halide Perovskite Photovoltaics: Background, Status, and Future Prospects. *Chem. Rev.* **2019**, *119*, 3036–3103; (b) Dou, L.; Yang, Y.; You, J.; Hong, Z.; Chang, W.-H.; Li, G.; Yang, Y. Solution-Processed Hybrid Perovskite Photodetectors with High Detectivity. Nat. Commun. 2014, 5, 5404; (c) Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M. J.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G. Perovskite Materials for Light Emitting Diodes and Lasers. Adv. Mater. 2016, 28, 6804-6834.

(3) Mitzi, D. B. Synthesis, Structure and Properties of Organic-Inorganic Perovskites and Related Materials. Prog. Inorg. Chem. 1999, 48, 1-121.

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(4) (a) Li, W.; Wang, Z.; Deschler, F.; Gao, S.; Friend, R. H.; Cheetham,

- A. K. Chemically Diverse and Multifunctional Hybrid Organic-Inorganic Perovskites. Nat. Rev. Mater. 2017, 2, 16099; (b) Saparov, B.; Mitzi, D. B. Organic-inorganic perovskites: structural versatility for functional materials design. Chem. Rev. 2016, 116, 4558-4596; (c) Manser, J. S.; Christmas, J. A.; Kamat, P. V. Intriguing Optoelectronic Properties of 10 Metal Halide Perovskites. Chem. Rev. 2016, 116, 12956-13008.
- (5) Deschler, F.; Price, M.; Pathak, S.; Klintberg, L. E.; Jarausch, D.-D.; 11 Higler, R.; Hüttner, S.; Leijtens, T.; Stranks, S. D.; Snaith, H. J.; Atatüre, 12 M.; Phillips, R. T.; Friend, R. H. High Photoluminescence Efficiency and 13 Optically Pumped Lasing in Solution-Processed Mixed Halide Perovskite Semiconductors. J. Phys. Chem. Lett. 2014, 5, 1421-1426. 14
- (6) Jain, P.; Ramachandran, V.; Clark, R. J.; Zhou, H. D.; Toby, B. H.; 15 Dalal, N. S.; Kroto, H. W.; Cheetham, A. K. Multiferroic Behavior 16 Associated with an Order-Disorder Hydrogen Bonding Transition in 17 Metal-Organic Frameworks (MOFs) with the Perovskite ABX3 Architecture. J. Am. Chem. Soc. 2009, 131, 13625-13627. 18
- (7) (a) You, Y. M.; Liao, W. Q.; Zhao, D. W.; Ye, H. Y.; Zhang, Y.; Zhou, 19 Q. H.; Niu, X. H.; Wang, J. L.; Li, P. F.; Fu, D. W.; Wang, Z. M.; Gao, S.; 20 Yang, K. L.; Liu, J. M.; Li, J. Y.; Yan, Y. F.; Xiong, R. G. An Organic-Inorganic Perovskite Ferroelectric with Large Piezoelectric Response. 21 Science 2017, 357, 306-309; (b) Liao, W.-Q.; Zhao, D.; Tang, Y.-Y.; 22 Zhang, Y.; Li, P.-F.; Shi, P.-P.; Chen, X.-G.; You, Y.-M.; Xiong, R.-G. A 23 molecular perovskite solid solution with piezoelectricity stronger than lead zirconate titanate. Science 2019, 363, 1206-1210. 24
- (8) (a) Huang, P.-J.; Taniguchi, K.; Miyasaka, H. Bulk photovoltaic effect 25 in a pair of chiral-polar layered perovskite-type lead iodides altered by 26 chirality of organic cations. J. Am. Chem. Soc. 2019, 141, 14520-14523; 27 (b) Ahn, J.; Lee, E.; Tan, J.; Yang, W.; Kim, B.; Moon, J. A New Class of Chiral Semiconductors: Chiral-Organic-Molecule-Incorporating Organic-28 Inorganic Hybrid Perovskites. Mater. Horiz. 2017, 4, 851-856; (c) Peng, 29 Y.; Yao, Y.; Li, L.; Wu, Z.; Wang, S.; Luo, J. White-light emission in a 30 chiral one-dimensional organic-inorganic hybrid perovskite. J. Mater. Chem. C 2018, 6, 6033-6037. 31
- (9) (a) Ahn, J.; Ma, S.; Kim, J.-Y.; Kyhm, J.; Yang, W.; Lim, J. A.; Kotov, 32 N. A.;
- 33 Moon, J. Chiral 2D Organic Inorganic Hybrid Perovskite with Circular Dichroism Tunable Over Wide Wavelength Range. J. Am. Chem. Soc. 34 2020, 142, 4206-4212; (b) Ma, J.; Fang, C.; Chen, C.; Jin, L.; Wang, J.; 35 Wang, S.; Tang, J.; Li, D. Chiral 2D perovskites with a high degree of 36 circularly polarized photoluminescence. ACS Nano 2019, 13, 3659-3665; 37 (c) Dang, Y.; Liu, X.; Sun, Y.; Song, J.; Hu, W.; Tao, X. Bulk Chiral Halide Perovskite Single Crystals for Active Circular Dichroism and 38 Circularly Polarized Luminescence. J. Phys. Chem. Lett. 2020, 11, 39 1689-1696; (d) Yuan, C.; Li, X.; Semin, S.; Feng, Y.; Rasing, T.; Xu, J. 40 Chiral Lead Halide Perovskite Nanowires for Second-Order Nonlinear Optics. Nano Lett. 2018, 18, 5411-5417; (e) Long, G.; Jiang, C.; Sabatini, 41 R.; Yang, Z.; Wei, M.; Quan, L. N.; Liang, Q.; Rasmita, A.; Askerka, M.; 42 Walters, G.; Gong, X.; Xing, J.; Wen, X.; Quintero-Bermudez, R.; Yuan, 43 H.; Xing, G.; Wang, X. R.; Song, D.; Voznyy, O.; Zhang, M.; Hoogland, S.; Gao, W.; Xiong, Q.; Sargent, E. H. Spin control in reduced-44 dimensional chiral perovskites. Nat. Photonics 2018, 12, 528-533; (f) Lu, 45 H.; Wang, J.; Xiao, C.; Pan, X.; Chen, X.; Brunecky, R.; Berry, J. J.; Zhu, 46 K.; Beard, M. C.; Vardeny, Z. V. Spin-dependent charge transport through 2D chiral hybrid lead-iodide perovskites. Sci. Adv. 2019, 5, eaay0571.
- 47 (10) (a) Dong, Y. Z.; Zhang, Y. P.; Li, X. Y.; Feng, Y. Q.; Zhang, H.; Xu, 48 J. L. Chiral Perovskites: Promising Materials toward Next-Generation 49 Optoelectronics. Small 2019, 15, 1970209; (b) Chen, C.; Gao, L.; Gao, W.; Ge, C.; Du, X.; Li, Z.; Yang, Y.; Niu, G.; Tang, J. Circularly polarized 50 light detection using chiral hybrid perovskite. Nat. Commun. 2019, 10, 51 1927. 52
- (11) (a) Li, P.-F.; Liao, W.-Q.; Tang, Y.-Y.; Qiao, W.; Zhao, D.; Ai, Y.; 53 Yao, Y.-F.; Xiong, R.-G. Organic enantiomeric high-T<sub>c</sub> ferroelectrics. Proc. Natl. Acad. Sci. U. S. A. 2019, 116, 5878-5885; (b) Zhang, H.-Y.; 54 Tang, Y.-Y.; Shi, P.-P.; Xiong, R.-G. Toward the targeted design of 55

molecular ferroelectrics: modifying molecular symmetries and homochirality. Acc. Chem. Res. 2019, 52, 1928-1938.

- (12) Scott, J. Applications of Modern Ferroelectrics. Science 2007, 315, 954-959.
- (13) (a) Gao, J.-X.; Zhang, W.-Y.; Wu, Z.-G.; Zheng, Y.-X.; Fu, D.-W. Enantiomorphic Perovskite Ferroelectrics with Circularly Polarized Luminescence. J. Am. Chem. Soc. 2020, 142, 4756-4761; (b) Ai, Y.; Chen, X. G.; Shi, P. P.; Tang, Y. Y.; Li, P. F.; Liao, W. Q.; Xiong, R. G., Fluorine Substitution Induced High T<sub>c</sub> of Enantiomeric Perovskite Ferroelectrics: (R)- and (S)-3-(Fluoropyrrolidinium)MnCl<sub>3</sub>. J. Am. Chem. Soc. 2019, 141, 4474-4479; (c) Tang, Y. Y.; Ai, Y.; Liao, W. Q.; Li, P. F.; Wang, Z. X.; Xiong, R. G. H/F-Substitution-Induced Homochirality for Designing High-T<sub>c</sub> Molecular Perovskite Ferroelectrics. Adv. Mater. 2019, 31. 1902163.

(14) Horiuchi, S.; Tokura, Y. Organic ferroelectrics. Nat. Mater. 2008, 7, 357-366.

(15) Hu, Y.; Florio, F.; Chen, Z.; Phelan, W. A.; Siegler, M. A.; Zhou, Z.; Guo, Y.; Hawks, R.; Jiang, J.; Feng, J.; Zhang, L.; Wang, B.; Wang, Y.; Gall, D.; Palermo, E. F.; Lu, Z.; Sun, X.; Lu, T.-M.; Zhou, H.; Ren, Y.; Wertz, E.; Sundararaman, R.; Shi, J. A chiral switchable photovoltaic ferroelectric 1D perovskite. Sci. Adv. 2020, 6, eaay4213.

- (16) (a) Li, L.; Liu, X.; Li, Y.; Xu, Z.; Wu, Z.; Han, S.; Tao, K.; Hong, M.; Luo, J.; Sun, Z. Two-Dimensional Hybrid Perovskite-Type Ferroelectric for Highly Polarization-Sensitive Shortwave Photodetection. J. Am. Chem. Soc. 2019, 141, 2623-2629; (b) Chen, X.-G.; Song, X.-J.; Zhang, Z.-X.; Li, P.-F.; Ge, J.-Z.; Tang, Y.-Y.; Gao, J.-X.; Zhang, W.-Y.; Fu, D.-W.; You, Y.-M.; Xiong, R.-G. Two-Dimensional Layered Perovskite Ferroelectric with Giant Piezoelectric Voltage Coefficient. J. Am. Chem. Soc. 2020, 142, 1077-1082; (c) Wang, S.; Liu, X.; Li, L.; Ji, C.; Sun, Z.; Wu, Z.; Hong, M.; Luo, J. An Unprecedented Biaxial Trilayered Hybrid Perovskite Ferroelectric with Directionally-Tunable Photovoltaic Effects. J. Am. Chem. Soc. 2019, 141, 7693-7697; (d) Hua, X. N.; Liao, W. Q.; Tang, Y. Y.; Li, P. F.; Shi, P. P.; Zhao, D.; Xiong, R. G. A Room-Temperature Hybrid Lead Iodide Perovskite Ferroelectric. J. Am. Chem. Soc. 2018, 140, 12296-12302; (e) Xu, W. J.; Li, P. F.; Tang, Y. Y.; Zhang, W. X.; Xiong, R. G.; Chen, X. M. A Molecular Perovskite with Switchable Coordination Bonds for High-Temperature Multiaxial Ferroelectrics. J. Am. Chem. Soc. 2017, 139, 6369-6375; (f) Chen, S.; Shang, R.; Wang, B. W.; Wang, Z. M.; Gao, S. An A-Site Solution Perovskite Series Mixed-Ammonium Solid of [(NH<sub>2</sub>NH<sub>3</sub>)<sub>x</sub>(CH<sub>3</sub>NH<sub>3</sub>)<sub>1-x</sub>][Mn(HCOO)<sub>3</sub>](x=1.00-0.67). Angew. Chem. Int. Ed. 2015, 54, 11093-11096; (g) Xiong, Y.-A.; Sha, T.-T.; Pan, Q.; Song, X.-J.; Miao, S.-R.; Jing, Z.-Y.; Feng, Z.-J.; You, Y.-M.; Xiong, R.-G. A Nickel(II) Nitrite Based Molecular Perovskite Ferroelectric. Angew. Chem., Int. Ed. 2019, 58, 8857-8861.
- (17) (a) Wu, Y.; Shaker, S.; Brivio, F.; Murugavel, R.; Bristowe, P. D.; Cheetham, A. K. [Am]Mn(H<sub>2</sub>POO)<sub>3</sub>: A New Family of Hybrid Perovskites Based on the Hypophosphite Ligand. J. Am. Chem. Soc. 2017, 139, 16999-17002; (b) Xu, W.-J.; Du, Z.-Y.; Zhang, W.-X.; Chen, X.-M. Structural Phase Transitions in Perovskite Compounds Based on Diatomic or Multiatomic Bridges. CrystEngComm 2016, 18, 7915-7928; (c) Sun, Y.-L.; Han, X.-B.; Zhang, W. Structural Phase Transitions and Dielectric Switching in a Series of Organic-Inorganic Hybrid Perovskites ABX<sub>3</sub> (X = ClO<sub>4</sub><sup>-</sup> or BF<sub>4</sub><sup>-</sup>). Chem. Eur. J. 2017, 23, 11126–11132; (d) Shi, C.; Ye, L.; Gong, Z.-X.; Ma, J.-J.; Wang, Q.-W.; Jiang, J.-Y.; Hua, M.-M.; Wang, C.-F.; Yu, H.; Zhang, Y. Two-Dimensional Organic-Inorganic Hybrid Rare-Earth Double Perovskite Ferroelectrics. J. Am. Chem. Soc. 2019, 142, 545-551

(18) (a) Zhang, W.; Xiong, R.-G. Ferroelectric metal-organic frameworks. Chem. Rev. 2012, 112, 1163-1195; (b) Shi, P. P.; Tang, Y. Y.; Li, P. F.; Liao, W. Q.; Wang, Z. X.; Ye, Q.; Xiong, R. G. Symmetry breaking in molecular ferroelectrics. Chem. Soc. Rev. 2016, 45, 3811-3827.

(19) Kleinman, D. A. Nonlinear dielectric polarization in optical media. Phys. Rev. 1962, 126, 1977.

(20) Chen, S.; Shang, R.; Hu, K.-L.; Wang, Z.-M.; Gao, S.  $[NH_2NH_3][M(HCOO)_3]$  (M = Mn<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup> and Mg<sup>2+</sup>): structural phase transitions, prominent dielectric anomalies and negative thermal expansion, and magnetic ordering. Inorg. Chem. Front. 2014, 1, 83-98.

