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A multiaxial lead-free two-dimensional organic-inorganic perovskite ferroelectric

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ABSTRACT

Two-dimensional (2D) hybrid organic-inorganic perovskites (HOIPs) have recently gained tremendous interest because of their unique features in contrast to the three-dimensional counterparts and the traditional 2D materials. However, although some 2D HOIP ferroelectrics have been achieved, the issue of toxic Pb and the uniaxial nature impede their further application. Herein, for the first time, we report a lead-free 2D HOIP multiaxial ferroelectric, [3,3-difluorocyclobutylammonium]₂CuCl₄ (1), which shows 4 ferroelectric axes and 8 equivalent polarization directions, more than those of the other 2D HOIP ferroelectrics and even the inorganic perovskite ferroelectric BaTiO₃ (3 ferroelectric axes and 6 equivalent polarization directions). 1 also
features a high Curie temperature of 380 K and exhibits remarkable thermochromism of color change from green-yellow to dark brown. To our knowledge, 1 is the first multiaxial lead-free 2D HOIP ferroelectric. This work sheds lights on exploring more excellent lead-free 2D HOIP ferroelectrics.

**Keywords:** ferroelectrics, organic-inorganic perovskites, multiaxial ferroelectrics, Curie temperature, thermochromism

**INTRODUCTION**

Perovskite-type materials have received remarkable attention all over the world since they have been discovered and investigated [1-3]. The large family of perovskites are acting as potential candidates for electronic and photoelectronic devices [4-6]. In recent years, the rapid development of three-dimensional (3D) CH$_3$NH$_3$PbI$_3$ based perovskite solar cells has aroused great research interest in the low-cost and easily solution-processable hybrid organic-inorganic perovskites (HOIPs) [7-10]. Among them, the two-dimensional (2D) lead halide HOIPs, which have the good moisture resistance, compositional diversity, quantum-well electronic structure, broadband emission, and layer-tunable photoelectronic properties in contrast to the 3D counterparts, are attracting increasing attention [11-14]. These features and the rich physical properties also make 2D HOIPs unique from the conventional 2D materials including graphene, graphdiyne, MoS$_2$, and WS$_2$ [15,16]. 2D HOIPs adopt the typical crystal structure of organic cationic layer alternating with the 2D inorganic anionic framework [11-14]. This structural feature provides a great opportunity for arousing the ferroelectricity [17,18], which shows a crucial role in ferroelectric random access memory, piezoelectric devices and capacitors [19-23]. Ferroelectricity was found in a number of lead halide 2D HOIPs [24-35], such as (4,4-diflorocyclohexylammonium)$_2$PbI$_4$ [24], (C$_5$H$_{10}$CHNH$_3$)$_2$PbBr$_4$ [25],
(C₆H₅CH₂NH₃)₂PbCl₄ [26], [CH₃(CH₂)₃NH₃]₂(CH₃NH₃)Pb₂Br₇ [27], and (C₄H₉NH₃)₂(NH₂CHNH₂)Pb₂Br₇ [28]. Some of them show excellent ferroelectric performance of high Curie temperature and large piezoelectric voltage coefficient [33,34]. However, the environmental toxicity of lead is an obstacle for their further applications. Within 2D HOIPs, the Pb(II) cation can be replaced by Sn(II), Ge(II), Cd(II), Mn(II), Fe(II), Cu(II) etc, while 2D HOIPs based on these metal cations are mainly investigated for the semiconducting property, photoluminescence, phase transitions, and magnetism [36]. Recently, (C₄H₉NH₃)₂(NH₃CH₃)Sn₃Br₁₀ was discovered as a potential ferroelectric without evidence of polarization switching [37], and Ye et al. reported the 2D organic-inorganic double perovskite ferroelectrics [(R)- and (S)-3-hydroxylquinuclidinium]₄KCe(NO₃)₈ [38]. Whereas, the lead-free 2D HOIP ferroelectrics remain very rare.

Regarding to the application of ferroelectric materials, multiaxial ferroelectrics with multiple ferroelectric axes and equivalent polarization directions are highly preferable in contrast to the uniaxial counterparts with one ferroelectric axes and two opposite polarization directions [39,40]. In the ferroelectric polycrystalline and thin-film sample, the more equivalent polarization directions allow easier and more effective polarization switching. The commercial ferroelectrics are generally multiaxial, and the multiaxial feature makes them widely used in the polycrystalline and thin-film form, as exampled by the inorganic perovskite BaTiO₃ with 3 ferroelectric axes and 6 equivalent polarization directions [39,40]. In this respect, however, most of the 2D HOIP ferroelectrics are only uniaxial or biaxial [24-35], which also greatly restricts their future applications. Especially, the lead-free [(R)- and (S)-3-hydroxylquinuclidinium]₄KCe(NO₃)₈ are uniaxial ferroelectrics [38].

Here, we reported a lead-free 2D Cu(II) halide HOIP multiaxial ferroelectric
[3,3-difluorocyclobutylammonium]$_2$CuCl$_4$ ([DF-CBA]$_2$CuCl$_4$, 1), which shows a $4/mnmFm$ ferroelectric phase transition at a high Curie temperature of 380 K, leading to 4 ferroelectric axes and 8 equivalent polarization directions, larger than those of the other 2D HOIP ferroelectrics and the BaTiO$_3$. Interestingly, 1 also presents prominent thermochromic behavior of color change from green-yellow to dark brown, which is not observed in the lead halide 2D HOIP ferroelectrics. To our knowledge, 1 is the first multiaxial lead-free 2D HOIP ferroelectric. This pioneering work throws light on exploring new excellent multiaxial lead-free 2D HOIP ferroelectrics with application prospects.

RESULTS AND DISCUSSION

We obtained single-crystals of 1 by slow evaporation of a methanol solution containing [3,3-difluorocyclobutylammonium]Cl and CuCl$_2$. Single-crystal X-ray diffraction experiments reveal that 1 crystallizes in the monoclinic polar $Cc$ space group (point group $m$ ($C_{1h}$)) at 293 K in the ferroelectric phase (FP) (Supplementary Table S1). The crystal structure contains inorganic [CuCl$_4$]$^{2-}$ layers of corner-sharing CuCl$_6$ octahedral separated by organic [DF-CBA]$^+$ bilayers (Fig. 1a), showing the 2D organic-inorganic A$_2$BX$_4$ perovskite structure [36], where the [DF-CBA]$^+$, Cu$^{2+}$, and Cl$^-$ ion corresponds to the A, B, and X site, respectively. Thus, 1 can be regarded as the 2D halide perovskite, similar to the case of [CH$_3$NH$_3$]$_2$CuCl$_4$ [41]. The CuCl$_6$ octahedron is Jahn-Teller distorted with two Cu–Cl bond lengths (3.1635 Å and 3.0523 Å) obviously longer than the other four ones (2.2583-2.3179 Å) (Supplementary Table S2). The alternate elongated Cu–Cl bonds of the Jahn-Teller distorted CuCl$_6$ octahedra are perpendicular to each other, showing an anti-ferrodistortive arrangement in the $bc$ plane (Supplementary Fig. S1), as found in [2,2’-(ethylenedioxy)bis(ethylammonium)]CuCl$_4$ [42]. The [DF-CBA]$^+$ cations are orientationally
ordered, of which the C–N bonds align along one single orientation (Fig. 1a). The polar [DF-CBA]$^+$ cation with electric dipole moment shows an orientational arrangement along the c axis with all the C–N groups of [DF-CBA]$^+$ cations aligning along the c axis (Supplementary Fig. S2). Such an orientational arrangement of polar cations will induce a polarization [26]. Between the inorganic and organic components, there are weak N–H···Cl hydrogen-bonding interactions (Supplementary Fig. S3a), in which the average donor-acceptor distance is 3.350 Å.

At 393 K in the paraelectric phase (PP), the crystal symmetry of 1 changes to the tetragonal centrosymmetric $P4_2/mmc$ space group (point group $4/mmm$ ($D_{4h}$)). The relationship between the unit cell of FP and PP is $a_{FP} \approx c_{PP}$, $b_{FP} \approx \sqrt{2} a_{PP}$, and $c_{FP} \approx \sqrt{2} b_{PP}$. In the crystal structure, both the inorganic and organic constituents get seriously disordered (Fig. 1b). The atomic coordinates of the four bridged Cl atoms of CuCl$_6$ octahedron were split into two positions (Fig. 1b and Supplementary Fig. S3b). The [DF-CBA]$^+$ cation exhibits a four-fold orientational disorder with the C−N bonds having four orientations because that it occupies the $2mm$ symmetry positions (Fig. 1b and Supplementary Fig. S3b). Thus, both the order-disorder transitions of the inorganic [CuCl$_4$]$^{2-}$ framework and the organic [DF-CBA]$^+$ cations contribute to the ferroelectric-to-paraelectric phase transition. In PP, the dipole moment of [DF-CBA]$^+$ cation cancels each other out because of the centrosymmetric crystal symmetry. We also confirm the structural phase transition of 1 by the variable-temperature powder X-ray diffraction (PXRD) experiments (Supplementary Fig. S4). The PXRD patterns at 293 K are consistent with the simulated ones from the crystal structure (Supplementary Fig. S4b) and show no obvious change with temperature increasing in FP. When the temperature increases to PP, the numbers of PXRD patterns reduce obviously, especially in the 2θ range from 16° to 24° (Supplementary Fig. S4a), which indicates a higher symmetry in PP. The
experimental PXRD patterns at 393 K also match the simulated ones from the crystal structure (Supplementary Fig. S4c).

Differential scanning calorimetry (DSC) experiments reveal that the ferroelectric-to-paraelectric phase transition of 1 occurs at $T_c = 380$ K (Fig. 2a). The phase transition is very reversible and repeatable as reflected from the DSC curves recorded in three heating/cooling cycles (Supplementary Fig. S5). Thermogravimetric analysis (TGA) curves show that 1 is thermally stable up to 480 K (Supplementary Fig. S6), which is much higher than the phase transition temperature of 380 K. The dielectric anomaly near $T_c$ in the temperature-dependent real part ($\varepsilon'$), loss (tan$\delta$), and imaginary part ($\varepsilon'' = \varepsilon' \times \tan\delta$) of the complex permittivity of 1 at 1 MHz further verifies this phase transition (Fig. 2b, Fig. 2b inset, and Supplementary Fig. S7). The $\varepsilon'$ at 1 kHz, 10 KHz, and 100 KHz shows obvious dielectric anomalies near 380 K as well (Supplementary Fig. S8). At lower frequencies, the dielectric anomalies are much remarkable and become more like a peak shape (Supplementary Fig. S8). The peak temperature of the dielectric anomalies shows no obvious shift from the frequency of 1 kHz to 1 MHz, showing no dielectric relaxations. We also employed the temperature-dependent second harmonic generation (SHG) signal to study the phase transition. The SHG intensity of 1 has a certain value of about a quarter of that of KDP (potassium dihydrogen phosphate) at 293 K in the FP, decreases to a zero value near $T_c$, and maintains zero values in the PP. This corresponds to the transition from the polar point group $m$ ($C_{1h}$) to a centrosymmetric 4/mmm ($D_{4h}$) one. According to Aizu notion [43], the phase transition in 1 is the 4/mmmFm type ferroelectric one. As Fig. 3a shows, from PP to FP, the symmetry breaks from 16 symmetry elements ($E$, $2C_4$, $C_2$, $2C'_2$, $2C''_2$, $i$, $2S_4$, $\sigma_h$, $2\sigma_v$, and $2\sigma_d$) in 4/mmm ($D_{4h}$) point group to 2 ones ($E$ and $\sigma_h$) in $m$ ($C_{1h}$) point group. Thus, 1 is a multiaxial ferroelectric with 4 ferroelectric axes and 8 equivalent polarization directions. It is noted
that the polarization directions of 1 are much more than those of other 2D HOIPs, most of which are uniaxial or biaxial ferroelectrics [24-35], and even more than the 6 polarization directions of typical inorganic perovskite ferroelectric BaTiO$_3$ (Fig. 3b) [39,40]. The multiaxial nature of 1 facilitates its applications in the thin film form [39,40].

We then recorded the polarization-electric filed ($P$-$E$) hysteresis loop of 1. As shown in Figure 2d, 1 presents a $P$-$E$ hysteresis loop obtained on the single-crystal sample along the $c$ axis at 328 K in the FP, directly proving the ferroelectricity. The saturate polarization ($P_s$) is estimated to be 0.29 $\mu$C/cm$^2$ from the loop, which is larger than that of the first molecular ferroelectric Rochelle Salt (0.25 $\mu$C/cm$^2$) [44]. We also calculated the $P_s$ of 1 based on the point charge mode (Supplementary Fig. S9). The experimental value is comparable to the calculated one (0.328 $\mu$C/cm$^2$).

We also characterized the domain structure of 1 on its thin film by piezoresponse force microscopy (PFM). The typical domain pattern was arranged in a stripe texture. An example was shown in Fig. 4. The stripe contrast can be clearly observed in both lateral and vertical amplitude images, in which the light and dark tones represent the local piezoresponse along the in-plane direction for lateral image and out-of-plane direction for vertical image. By comparison of the phase images, a uniform phase in the vertical phase image is seen, contrastingly, in the lateral phase image the stripe domains were observed. The phase anisotropy of the vertical and lateral PFM modes indicates the existence of non-180° domain walls in the thin film, which thus reveals that 1 is a multiaxial ferroelectric.

Figure 5a and b respectively display the pristine vertical PFM amplitude and phase images of a region of 20 × 20 $\mu$m, together with the surface topography image shown in Fig. 5c. By locally poling the red-boxed region marked in Fig. 5e with positive voltage of +25 V, we found that a new
domain was generated through the polarization switching. Next, a -20 V, 1 s duration voltage pulse was applied at the position “×” in the new domain. As a result, the partial of the new domain was switched back with 180˚ phase shift. Furthermore, local ferroelectric hysteresis loops can also be recorded by switching spectroscopy PFM measurements. A set of DC voltage pulses up to ±20 V were applied to switching the polarization underneath the PFM tip, with a 5V ac tip bias applied to record the corresponding piezoelectric amplitude and phase signal. As shown in Fig. 5f, 180˚ phase reversal occurs when a coercive voltage is exceeded. At the same time, hysteresis amplitude-bias butterfly loops were observed (Fig. 5i). Overall, our PFM measurements provide robust proof of the switchable polarization in 1.

Interestingly, distinct from the 2D lead halide perovskite ferroelectrics, 1 exhibits thermochromic behaviors. Its crystal changes color obviously, reversibly and repeatedly from yellow-green at 293K to dark brown color at 393 K (Fig. 6a). The UV-Vis absorption spectra at 293 K shows that 1 mainly absorbs light less than about 530 nm, matching with its yellow-green appearance. It is worth noting that there is a minor and broad absorption peak at around 750 nm in the absorption spectra, which is commonly found 2D copper (II) chloride HOIP perovskites like [CH$_3$NH$_3$]$_2$CuCl$_4$ [41], and this absorption peak can be assigned to the $d$-$d$ electronic transitions in the Cu$^{2+}$ ions with the 3$d^9$ electronic configuration [41]. When the temperature increases, the main absorption band in the UV-Vis absorption spectra shows a remarkable red shift from 293 K to 393 K (Fig. 6a). We also recorded the UV-Vis absorption spectra at different temperatures (Supplementary Fig. S10). The main absorption peaks at around 257 nm and 354 nm at 293 K show very slight red-shifts when the temperature increases to 393 K. For the main absorption peak at around 435 nm at 293 K, it presents minor red-shifts with temperature increasing below the phase transition temperature ($T_c$) of 380 K,
and shows a relatively remarkable red-shift from 373 K below the $T_c$ to 393 K above $T_c$. When the temperature increases, the absorption edges of main visible absorption band at around 524 nm at 293 K also shows a remarkable red-shift from 373 K to 393 K. This indicates that the thermochromism of \textbf{1} is associated with the phase transition, as found in other thermochromic organic–inorganic Cu(II) halides showing phase transitions, in which the thermochromism is mainly related to the coordination environment change of copper (II) ion during the phase transition [45-47]. In \textbf{1}, the out-plane Cl–Cu–Cl bond angles of 86.43°–94.43° at 293 K in FP become 90.00° at 393 K in PP (Supplementary Fig. S11 and Supplementary Table S2). The average long in-plane Cu–Cl bond distance of 3.1515 Å, the average short in-plane Cu–Cl bond distance of 2.259 Å, and the out-plane Cu–Cl bond distances of 2.2321 Å in PP is also obviously different from those in FP (3.1075 Å, 2.3155 Å, and 2.2601 Å and 2.2583 Å, respectively). The changes of Cl–Cu–Cl bond angles and Cu–Cl bond distance show the geometry change of CuCl$_6$ octahedron, which contributes to the thermochromism.

In order to investigate the underlying cause of thermochromism, the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of CuCl$_6$ octahedral configurations in FP and PP are calculated (Fig. 6b). The HOMO and LUMO in PP display distinct variation with them in FP. The resultant energy gap shifted from 0.1458 Ha (Hartree) in the FP to 0.1164 Ha of PP. The large energy gap change could be attributed to the remarkable configuration change of CuCl$_6$ octahedral. Accordingly, the absorption edge will have a red-shift tendency in the heating process from FP to PP, which is consistent with the experimental variable-temperature UV–vis absorption spectra.
CONCLUSION

In summary, we have presented a lead-free 2D HOIP ferroelectric, [3,3-difluorocyclobutylammonium]₂CuCl₄, which undergoes a $4/mmmFm$ type ferroelectric phase transition at 380 K. Strikingly, 1 is a multiaxial ferroelectric with 8 polarization directions, much more than those of 2D lead halide perovskite ferroelectrics, fascinating its application in the thin film form. This is the first example of 2D lead-free perovskite multiaxial ferroelectric. Moreover, during the ferroelectric-to-paraelectric phase transition, 1 shows remarkable thermochromism of color change from green-yellow to dark brown. This work opens up a pathway to construct multiaxial lead-free 2D perovskite ferroelectrics.

METHODS

Sample preparation

The [3,3-difluorocyclobutylammonium]Cl ([DF-CBA]Cl) and CuCl₂ are commercially available. [DF-CBA]Cl (10 mmol) and CuCl₂ (5 mmol) were completely dissolved in methanol (100 ml). Slow evaporation of the solvent at room temperature obtains the crystals of [DF-CBA]₂CuCl₄ (yield, 98.5%). Single-crystal X-ray diffraction experiments reveal that the obtained crystals have the formula of [DF-CBA]₂CuCl₄ (Supplementary Table S1). The phase purity of the as-grown crystals was confirmed by PXRD (Supplementary Fig. S4b). We prepared the thin film of [DF-CBA]₂CuCl₄ by spreading 10 µL precursor solution (100 mg as grow-crystals in 1 mL methanol) on ITO coated glass substrate. Annealing the substrate at 313 K obtains the thin film sample.

Characterization methods

Methods of XRD, DSC, dielectric, SHG, $P-E$ loop, PFM, and UV-vis absorption spectra
measurements were described in detail previously [26,32]. The HOMO and LUMO are calculated at 
b3lyp/aug-cc-pVTZ level.

Accession codes

The structures have been deposited at the Cambridge Crystallographic Data Centre (deposition 
numbers: CCDC 1982768-1982769).

SUPPLEMENTARY DATA

Supplementary data are available at NSR online.

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AUTHOR CONTRIBUTIONS

X.L. and R.-G.X. proposed and supervised the project. X.L. and R.-G.X. designed research. C.-R.H. 
synthesized the sample. C.-R.H., X.-G.C., X.-J.S. and Z.-X.Z. carried out the characterizations. All 
authors analyzed the data, discussed the results, and prepared the paper.

Conflict of interest statement. None declared.
REFERENCES

1. Tejuca LG and Fierro JL. Properties and applications of perovskite-type oxides. New York: CRC Press, 1993.

2. Li J, Zhong G and Xie S et al. Large-scale multiferroic complex oxide epitaxy with magnetically switched polarization enabled by solution processing. Natl Sci Rev 2020; 7: 84-91.

3. Lu C, Wu M and Lin L et al. Single-phase multiferroics: new materials, phenomena, and physics. Natl Sci Rev 2019; 6: 653-68.

4. Li W, Wang Z and Deschler F et al. Chemically diverse and multifunctional hybrid organic-inorganic perovskites. Nat Rev Mater 2017; 2: 16099.

5. Saparov B and Mitzi DB. Organic-inorganic perovskites: structural versatility for functional materials design. Chem Rev 2016; 116: 4558-96.

6. Li JF, Li L and Zhang X et al. Practical high-performance lead-free piezoelectrics: structural flexibility beyond utilizing multiphase coexistence. Natl Sci Rev 2020; 7: 355-65.

7. Li D, Shi J and Xu Y et al. Inorganic-organic halide perovskites for new photovoltaic technology. Natl Sci Rev 2018; 5: 559-76.

8. Jena AK, Kulkarni A and Miyasaka T. Halide perovskite photovoltaics: background, status, and future prospects. Chem Rev 2019; 119: 3036-103.

9. Stoumpos CC and Kanatzidis MG. Halide perovskites: poor man’s high-performance semiconductors. Adv Mater 2016; 28: 5778-93.

10. Manser JS, Christmas JA and Kamat PV. Intriguing optoelectronic properties of metal halide perovskites. Chem Rev 2016; 116: 12956-3008.

11. Dou L, Wong AB and Yu Y et al. Atomically thin two-dimensional organic-inorganic hybrid perovskites. Science 2015; 349: 1518-21.

12. Tsai H, Nie W and Blancon JC et al. High efficiency two-dimensional ruddlesden-popper perovskite solar cells. Nature 2016; 536: 312-6.

13. Proppe AH, Quintero-Bermudez R and Tan H et al. Synthetic control over quantum well width distribution and carrier migration in low-dimensional perovskite photovoltaics. J Am Chem Soc 2018; 140: 2890-6.
14. Mao L, Guo P and Kepenekian M et al. Structural diversity in white-light emitting hybrid lead bromide perovskites. *J Am Chem Soc* 2018; **140**: 13078-88.

15. Chen S and Shi G. Two-dimensional materials for halide perovskite-based optoelectronic devices. *Adv Mater* 2017; **29**: 1605448.

16. Zhong T, Li X and Wu M et al. Room-temperature multiferroicity and diversified magnetoelectric couplings in 2D materials. *Natl Sci Rev* 2020; **7**: 373-80.

17. Li LN, Sun ZH and Wang P et al. Tailored engineering of an unusual \((\text{C}_4\text{H}_9\text{NH}_3)_{2}(\text{CH}_3\text{NH}_3)_{2}\text{Pb}_3\text{Br}_{10}\) two-dimensional multilayered perovskite ferroelectric for a high performance photodetector. *Angew Chem Int Ed* 2017; **56**: 12150-4.

18. Wu ZY, Ji CM and Li LN et al. Alloying \(n\)-butylamine into \(\text{CsPbBr}_3\) to give a two-dimensional bilayered perovskite ferroelectric material. *Angew Chem Int Ed* 2018; **57**: 8140-3.

19. Scott J. Applications of modern ferroelectrics. *Science* 2007; **315**: 954-9.

20. Zhu S. Novel ferroelectric tunnel junctions for nonvolatile memories. *Natl Sci Rev* 2014; **1**: 167-8.

21. Wang ZM and Gao S. Can molecular ferroelectrics challenge pure inorganic ones? *Natl Sci Rev* 2014; **1**: 25-6.

22. Zhu J, Huang F and Li Y et al. Dynamics and manipulation of ferroelectric domain walls in bismuth ferrite thin films. *Natl Sci Rev* 2020; **7**: 278-84.

23. Liu Y, Seidel J and Li J. Multiferroics under the tip: probing magnetoelectric coupling at the nanoscale. *Natl Sci Rev* 2019; **6**: 626-8.

24. Sha TT, Xiong YA and Pan Q et al. Fluorinated 2D lead iodide perovskite ferroelectrics. *Adv Mater* 2019; **31**: 1901843.

25. Ye HY, Liao WQ and Hu CL et al. Bandgap engineering of lead-halide perovskite-type ferroelectrics. *Adv Mater* 2016; **28**: 2579-86.

26. Liao WQ, Zhang Y and Hu CL et al. A lead-halide perovskite molecular ferroelectric semiconductor. *Nat Commun* 2015; **6**: 7338.

27. Li L, Liu X and Li Y et al. Two-dimensional hybrid perovskite-type ferroelectric for highly polarization-sensitive shortwave photodetection. *J Am Chem Soc* 2019; **141**: 2623-9.

28. Li LN, Shang XY and Wang SS et al. Bilayered hybrid perovskite ferroelectric with giant two-photon absorption. *J Am Chem Soc* 2018; **140**: 6806-9.
29. Zhang HY, Song XJ and Chen XG et al. Observation of vortex domains in a two-dimensional lead iodide perovskite ferroelectric. *J Am Chem Soc* 2020; **142**: 4925-31.

30. Wang S, Liu X and Li L et al. An Unprecedented biaxial trilayered hybrid perovskite ferroelectric with directionally-tunable photovoltaic effects. *J Am Chem Soc* 2019; **141**: 7693-7.

31. Liu X, Wang S and Long P et al. Polarization-driven self-powered photodetection in a single-phase biaxial hybrid perovskite ferroelectric. *Angew Chem Int Ed* 2019; **58**: 14504-8.

32. Yang CK, Chen WN and Ding YT et al. The first 2D homochiral lead iodide perovskite ferroelectrics: \([R-\text{and} S-1-(4-chlorophenyl)ethylammonium}\)\(_2\)PbI\(_4\). *Adv Mater* 2019; **31**: 1808088.

33. Shi PP, Lu SQ and Song XJ et al. Two-dimensional organic-inorganic perovskite ferroelectric semiconductors with fluorinated aromatic spacers. *J Am Chem Soc* 2019; **141**: 18334-40.

34. Chen XG, Song XJ and Zhang ZX et al. Two-dimensional layered perovskite ferroelectric with giant piezoelectric voltage coefficient. *J Am Chem Soc* 2020; **142**: 1077-82.

35. Jia F, Hu S and Xu S et al. Persistent spin-texture and ferroelectric polarization in 2D hybrid perovskite benzylammonium lead-halide. *J Phys Chem Lett* 2020; **11**: 5177-83.

36. Mao L, Stoumpos CC and Kanatzidis MG. Two-dimensional hybrid halide perovskites: principles and promises. *J Am Chem Soc* 2019; **141**: 1171-90.

37. Li L, Liu X and He C et al. A potential Sn-based hybrid perovskite ferroelectric semiconductor. *J Am Chem Soc* 2020; **142**: 1159-63.

38. Shi C, Ye L and Gong ZX et al. Two-dimensional organic-inorganic hybrid rare-earth double perovskite ferroelectrics. *J Am Chem Soc* 2019; **142**: 545-51.

39. Tang YY, Li PF and Liao WQ et al. Multiaxial molecular ferroelectric thin films bring light to practical applications. *J Am Chem Soc* 2018; **140**: 8051-9.

40. Ye HY, Ge JZ and Tang YY et al. Molecular ferroelectric with most equivalent polarization directions induced by the plastic phase transition. *J Am Chem Soc* 2016; **138**: 13175-8.

41. Cortecchia D, Dewi HA and Yin J et al. Lead-free MA\(_2\)CuCl\(_x\)Br\(_{4-x}\) hybrid perovskites. *Inorg Chem* 2016; **55**: 1044-52.

42. Jaffe A, Lin Y and Mao W L et al. Pressure-induced conductivity and yellow-to-black piezochromism in a layered Cu–Cl hybrid perovskite. *J Am Chem Soc* 2015; **137**: 1673-8.

43. Aizu K. Possible species of “ferroelastic” crystals and of simultaneously ferroelectric and ferroelastic crystals. *J Phys Soc Jpn* 1969; **27**: 387-96.
44. Zhang W and Xiong RG. Ferroelectric metal-organic frameworks. *Chem Rev* 2012; **112**: 1163–95.

45. Willett RD, Haugen JA and Lebsack J *et al*. Thermochromism in copper(II) chlorides. coordination geometry changes in CuCl$_4^{2-}$ anions. *Inorg Chem* 1974; **13**: 2510-3.

46. Sun B, Liu XF and Li XY *et al*. Reversible thermochromism and strong ferromagnetism in two-dimensional hybrid perovskites. *Angew Chem Int Ed* 2020; **59**: 203-8.

47. Liu JC, Liao WQ and Li PF *et al*. A molecular thermochromic ferroelectric. *Angew Chem Int Ed* 2019; **59**: 3495-9.
Figure 1. Packing views of the crystal structures of 1 at (a) 293 K and (b) 393 K.
Figure 2. Ferroelectricity and related properties of 1. (a) DSC curves. (b) Temperature-dependent $\varepsilon'$ at 1 MHz upon heating. Inset: Temperature-dependent tan$\delta$ at 1 MHz upon heating. (c) Temperature-dependent SHG intensity upon heating. Inset, SHG signals of KDP and 1 at 293 K. (d) Ferroelectric hysteresis loop measured on the single-crystal sample along the $c$ axis at 328 K by using the double-wave method.
Figure 3. (a) Symmetry change between the PP and FP in 1. (b) Comparison of the polarization directions in BaTiO$_3$ and 1.
Figure 4. PFM imaging of domain pattern in the thin film of 1. Lateral (a) and vertical (b) PFM amplitude images. Lateral (c) and vertical (d) PFM phase images.
Figure 5. Polarization switching experiments for the thin film of 1. Initial PFM amplitude (a), PFM phase (b) and topographic (c) images of a region of 20 × 20 µm. PFM amplitude (d) and phase (e) images after applying voltage of +25 V on the red-boxed region. PFM amplitude (g) and phase (h) images after applying -20 V voltage pulse of 1 s duration on the point ×. PFM switching spectroscopy showing square-like phase loops (f) and butterfly-like amplitude loops (i).
Figure 6. (a) Crystal (size: 1.1×0.9×0.5 mm$^3$) color and solid-state UV-Vis absorption spectra of 1 at 293 K and 393 K. (b) The HOMO and LUMO of CuCl$_6$ octahedral configurations in FP and PP of 1.