Ferroelastic-switching-driven large shear strain and piezoelectricity in a hybrid ferroelectric

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Materials that can produce large controllable strains are widely used in shape memory devices, actuators and sensors⁹–¹⁰, and great efforts have been made to improve the strain output⁹–¹⁰. Among them, ferroelastic transitions underpin giant reversible strains in electrically driven ferroelectrics or piezoelectrics and thermally or magnetically driven shape memory alloys⁹–¹⁰. However, large-strain ferroelastic switching in conventional ferroelectrics is very challenging, while magnetic and thermal controls are not desirable for practical applications. Here we demonstrate a large shear strain of up to 21.5% in a hybrid ferroelectric, C₆H₅N(CH₃)₃CdCl₃, which is two orders of magnitude greater than that in conventional ferroelectric polymers and oxides. It is achieved by inorganic bond switching and facilitated by structural confinement of the large organic moieties, which prevents undesired 180° polarization switching. Furthermore, Br substitution can soften the bonds, allowing a sizable shear piezoelectric coefficient (dₛ ≈ 4,830 pm V⁻¹) at the Br-rich end of the solid solution, C₆H₅N(CH₃)₃CdBr₃Cl₁₋ₓ at the Br-rich end of the solid solution. C₆H₅N(CH₃)₃CdBr₃Cl₁₋ₓ. The electromechanical properties of these compounds suggest their potential in lightweight and high-energy-density devices, and the strategy described here could inspire the development of next-generation piezoelectrics and electroactive materials based on hybrid ferroelectrics.

The archetype of shape memory alloys, NiTi, can produce a strain of 6–8% from a temperature-induced reversible phase transition⁹. Other shape memory alloys can be triggered by magnetic fields. NiMnGa, for instance, shows up to 10% shear strain due to twin boundary movements under a magnetic field⁹. Perovskite piezoelectric oxides can achieve strains above 0.1% at morphotropic phase boundaries¹¹. Through point-defect engineering and/or ferroelastic domain switching, ferroelectric single crystals show strains up to 0.75% in aged BaTiO₃ (ref. ¹), while a maximum strain up to 1.7% was recorded in lead-based relaxors. For polymer systems, various stimuli have been explored to generate strains, including change in pH, temperature, light, moisture, and magnetic and electric fields¹². Owing to their structural flexibility, the strain response of some polymers, for example, elastomers, can even surpass 100% (ref. ¹³).

However, although many materials are available for various applications, very few simultaneously satisfy the requirements of large strain, high energy density and high speed. For example, shape memory alloys can produce large stress and medium strain, but the actuation output is always at a low speed¹⁴. Piezoelectric oxides can generate large stress at high speed, but the strain response is much lower than that of other materials. Polymers, by contrast, produce the largest strain while their actuation stress is one to two orders of magnitude smaller (2 MPa on average)¹⁵. Organic–inorganic hybrid ferroelectrics (OIHFs) consist of inorganic frameworks filled with organic moieties. Thus, they can take advantage of both the lightweight, flexible organic moiety and the mechanically strong and tough inorganic backbone, producing large strain with high energy/power output¹⁶. In recent years, various OIHFs have been designed and investigated; in particular, great progress has been made towards piezoelectric and electrostrictive applications¹⁷–¹⁹. The piezoelectric responses of some OIHFs have even surpassed those of traditional oxide ferroelectrics such as BaTiO₃, Pb(Zr, Ti)O₃ (PZT)²⁰. The multiaxial nature of these OIHFs implies that ferroelastic switching may lie at the core of the enhanced piezoelectricity¹⁷. However, direct proof of deterministic control of ferroelastic switching is still lacking.

The ferroelectricity in most OIHFs originates from the off-centre ordering of the positively charged organic moieties, which link with the inorganic frameworks through hydrogen bonds and van der Waals interactions. The reversal of the spontaneous polarization sometimes requires a complete flip of the large organic moiety, in stark contrast to oxide ferroelectrics, where polarization switching only involves relatively small displacement of the ions. It is thus possible to suppress the strain-equivalent 180° polarization switching in OIHFs with large molecular moiety owing to the high energy barrier and promote ferroelastic switching with large strain response. Following this strategy, we synthesize and investigate a hybrid ferroelectric, C₆H₅N(CH₃)₃CdCl₃·(PTMA)CdCl₃, which produces colossal ferroelastic shear strain that is around two orders of magnitude greater than that of lead-based piezoelectrics and larger than that of all shape memory alloys reported thus far. The non-volatile, reversible strain is attributed to macroscopic ferroelastic switching reflecting atomic-level lattice distortions, owing to the structural confinement effect. Furthermore, we demonstrate that Br substitution effectively softens the bonds and flattens the switching energy landscape, leading to large shear piezoelectric response at the Br-rich end of the solid solution (PTMA)CdBr₃Cl₁₋ₓ. X-ray diffraction (XRD) and differential scanning calorimetry (DSC) measurements were carried out to investigate the crystal structures and phase transitions of (PTMA)CdBr₃Cl₁₋ₓ. The lattice
constants of the compounds increase continuously from Cl to Br (Table 1 and Supplementary Fig. 1), while the phase transition temperature keeps decreasing from >180 °C (decomposition temperature) to 19 °C (Supplementary Fig. 2). However, no structural transition is induced by Br substitution. Powder XRD refinements indicate that the solid solutions all crystallize in the monoclinic $Cc$ space group in the low-temperature phase (LTP) and the orthorhombic $Ama_2$ space group in the high-temperature phase (HTP) (Table 1 and Supplementary Table 1), which can be described by the Aizu notation of $mm2Fm$ among the 88 ferroelectric transition species. In the LTP, (PTMA)CdBr$_3$$_{x}$Cl$_{3(1-x)}$ consists of PTMA organic moieties and a scaffold of 1D edge-sharing cadmium halide (CdX$_5$)$^-$ hexahedra (Fig. 1a and Supplementary Figs. 3, 4 for pure Cl, Br and mixed halide structures, respectively). They are connected via hydrogen bonds between the methyl group and the halide anions. In the HTP, the longest Cd–X bond of the hexahedron breaks, transforming it into a corner-sharing CdX$_4$$^-$ tetrahedron. In the meantime, order–disorder phase transition is triggered in the organic part with two degenerate positions and the restoration of mirror symmetry with respect to the (001) plane (Supplementary Text 1).

The ferroelectric polarization of (PTMA)CdBr$_3$$_{x}$Cl$_{3(1-x)}$ in the LTP can be understood by regarding N and Cd sites as the centres of positive and negative charges in the unit cell, respectively. As shown in Fig. 1c, the spontaneous polarization has components along both the $a$ axis and the $c$ axis, as confirmed by in-plane piezoresponse force microscopy (PFM) (Supplementary Fig. 5), and is in accordance with the monoclinic symmetry. However, owing to the large size of the organic moiety and confined space between the inorganic chains, a 180° reversal of the polarization is energetically unlikely. This is evidenced by the fact that the polarization along the $a$ axis persists even in the HTP. Fortunately, polarization switching along the $c$ axis is not hindered by the structure, which will rotate the polarization vector and generate large shear strain as shown in Fig. 1c. Experimentally, polarization–electric field ($P–E$) hysteresis loops can only be obtained along the $c$ axis, while no polarization switching is observed along the $a$ axis prior to electrical breakdown. The unique polarization switching path is consistent with the $mm2Fm$ Aizu notation, suggesting that symmetry breaking across the phase transition occurs only along one axis, as evidenced by the dielectric anomaly (Supplementary Fig. 6).

| Br amount (%) | 0 | 15 | 29 | 45 | 63 | 70 | 77 | 80 | 90 |
|--------------|---|----|----|----|----|----|----|----|----|
| $a$ (Å)      | 12.7541 | 12.8262 | 12.8497 | 12.8960 | 12.9338 | 12.9763 | 12.9909 | 13.0015 | 13.0465 |
| $b$ (Å)      | 14.5035 | 14.5961 | 14.6257 | 14.6785 | 14.7126 | 14.7458 | 14.7443 | 14.7601 | 14.7827 |
| $c$ (Å)      | 7.1515  | 7.2275  | 7.2554  | 7.3168  | 7.3650  | 7.4153  | 7.4261  | 7.4567  | 7.5058  |
| $\beta$ (%)  | 96.307  | 95.910  | 95.823  | 95.506  | 95.282  | 94.985  | 94.985  | 95.035  | 95.000  | 94.841  |
| Volume (Å$^3$) | 1,314.86 | 1,345.89 | 1,356.50 | 1,378.63 | 1,395.54 | 1,413.54 | 1,416.92 | 1,425.52 | 1,442.43 |
| Space group  | $Cc$ | $Cc$ | $Cc$ | $Cc$ | $Cc$ | $Cc$ | $Cc$ | $Cc$ | $Cc$ |

Fig. 1 | Crystal structures and photos of (PTMA)CdCl$_3$ in two different ferroelastic states. a, Perspective of crystallographic structure along the 1D chain (c) direction. b, Experimental setup for the shear strain and piezoelectricity measurements. Silver paste is applied on the $ab$ planes of the crystal as electrodes, and the electric field is applied along the 1D chain (c) direction. The coordinate numbers denote the Voigt notation of the strain tensor. c, Top: illustration of structural units in the two ferroelastic states and structure confinement effect for ferroelectric/ferroelastic switching. The yellow and green arrows indicate the polarization directions. Bottom: photos of a bulk single crystal poled to the two ferroelastic states by the electric field, showing a macroscopic shear strain in good correlation with the unit cell distortion.
Remarkably, upon polarization switching, the macroscopic tilting angle of the (PTMA)CdCl₃ crystal exhibits an appreciable change (~12.8°) that perfectly correlates with the unit cell distortion (Δβ = 12.6°) (Fig. 1c, Supplementary Videos 1 and 2), which translates to a shear strain \( S = \tan(\Delta \beta) \) of ~22%. Quantitative polarization and shear strain measurements were performed on the solid solutions by simultaneously recording the \( P-E \) and strain–electric field (\( S-E \)) hysteresis loops using the setup shown in Fig. 1b (details in Methods). Note that the measurements were conducted at elevated temperatures to facilitate the polarization switching (Supplementary Fig. 7), as commonly practiced for hybrid ferroelectrics. As shown in Fig. 2a, with increasing Br content, the remanent polarization \( P_r \) decreases monotonically from 3.6 \( \mu \)C cm\(^{-2} \) to 3.0 \( \mu \)C cm\(^{-2} \), which is in good agreement with the calculated polarizations of 3.7 \( \mu \)C cm\(^{-2} \) for the pure Cl compound and 2.9 \( \mu \)C cm\(^{-2} \) for the Br counterpart (Supplementary Text 2). Additionally, Br substitution apparently reduces the energy barrier for polarization switching, as indicated by the reduction of the critical temperature for switching and the coercive field. Shear strain \( (S) \) in this case is defined as \( S = \tan(\Delta \beta) \cdot d/H \), where \( d \) is the shear-strain-induced movement of the upper surface, \( H \) is the height of the sample and \( \Delta \beta \) is the shear angle (Supplementary Text 3). As shown in Fig. 2b, the reversible shear strain hits a record-breaking value of ~21.5% for the pure Cl compound, and decreases with increasing Br content, which is in good agreement with the smaller \( \beta \) angle in Br-rich compounds (Table 1). Given that the shear modulus \( C_{55} \) of (PTMA)CdCl₃ is around 5.8 GPa based on our first-principles calculations (Supplementary Text 2), we estimate a stress output of 40 MPa and a volumetric energy density of 4.2 MJ m\(^{-3} \). In Fig. 2c, we compare the reported actuation strain and the volumetric energy density for various material systems (details in Supplementary Table 2). The maximum shear strain of (PTMA)CdCl₃ is around two orders of magnitude greater than those of conventional ferroelectrics, surpassing those of all the reported shape memory alloys. Note that most electroactive polymers (EAPs) produce strains based on the Maxwell stress, and the electric field
Fig. 3 | Large-signal piezoelectric properties of (PTMA)CdBr$_2$Cl$_{3-x}$x. 

**a**, Unipolar S–E curves of the solid solution series at 2 Hz after pre-poling. 

**b**, Electric-field-dependent unipolar S–E curves of (PTMA)CdBr$_{2.7}$Cl$_{0.3}$ at 2 Hz. 

**c**, Contour plot of the large-signal $d_{35}^*$ versus electric field and frequency. 

**d**, A comparison of shear piezoelectric coefficients of different ferroelectric materials (references in Supplementary Table 3). Note that our sample shows a range of piezoelectric coefficients owing to the electric field and frequency dispersion. The values of Pb-based relaxors depend on the composition and domain configuration. 

**e**, A comparison between the bipolar shear strain hysteresis loop of (PTMA)CdCl$_3$ and the typical butterfly longitudinal strain curve of PMN-PT on a logarithmic scale. 

**f**, A comparison between the unipolar shear strain responses of (PTMA)CdBr$_{2.7}$Cl$_{0.3}$ and PMN-PT. The slopes of the linear fits are the large-signal piezoelectric coefficients.
required is of the order of MV cm⁻¹, which is much larger than the field used here. Further, for temperature-driven shape memory alloys (TSMAs) and shape memory polymers (SMPs), the response time is very long compared to our material (Supplementary Video 3). Therefore, the appropriate comparison should be with ferroelectric oxides (FE oxides), piezoelectric polymers and magnetically driven shape memory alloys (MSMAs), and (PTMA)CdCl₃ outperforms all of them.

Furthermore, with Br substitution, the lattice is softened considerably and large-shear piezoelectric response is achieved in Br-rich compounds. Unipolar piezoelectric response was measured for the solid solution series that have been pre-poled using the same experimental setup as that shown in Fig. 1b. Following Voigt notation, the piezoelectric coefficient measured in our setup is e₁₃ (ref. 79), which can be calculated by 
\[ e_{13} = S_{13}/E_{p} \]
that is, the slope of the S–E curves. Owing to the nonlinearity and hysteresis of the curve, the so-called 'large-signal' piezoelectric coefficient e₁₃* approximates S₁₃/Eₚ₉ (refs. 79,80) (Supplementary Text 3). As shown in Fig. 3a, e₁₃* increases monotonically with further Br substitution and reaches a maximum value of around 4,830 pm V⁻¹ for a 90% Br compound at low frequency (2 Hz) and under a large field (6 kV cm⁻¹). The shear piezoelectric coefficient is higher than those of recently discovered organic²⁸ hybrid piezoelectrics²⁸ as well as other classical oxide piezoelectrics (Fig. 3d)²⁴, and comparable to those of top-performing single-crystal relaxors²⁸. The greatly enhanced piezoelectric response in Br-rich crystals is attributed to the chemical-substitution-induced bond softening. This not only increases the intrinsic piezoelectricity of the compound but also enhances the extrinsic contribution of ferroelastic domain wall motion (switching) to the electromechanical response²⁵,²⁶. This is evidenced by the obvious field and frequency dependence of the piezoelectric behavior observed in the 90% Br sample (Fig. 3b,c), which correlates with the Rayleigh-like behaviour of the dielectric response (Supplementary Figs. 9 and 10)²¹. By examining the maximum strain in Fig. 2b and the monoclinic angle in Table 1, we can find that the pure Cl sample was poled into an almost single-domain state, while the Br-rich samples were not. Under a large field (along the same direction as the pre-poling field) at low frequency, the back-switched ferroelastic domains are activated again and contribute to the observed piezoelectric response. However, the involvement of ferroelastic switching inevitably leads to the hysteresis effect, which could be alleviated via targeted chemical engineering to achieve relaxor-like properties²²,²³. The unique electromechanical behaviour of our OHF is highlighted by a direct comparison with the classic oxide ferroelectric relaxor, Pb(Mg₀.₃₃Nb₀.₆₇)O-0.3PbTiO₃ (PMN-PT) single crystal (Fig. 3e,f and Supplementary Fig. 8). The asymmetric bipolar S–E curve reflects the ferroelastic-switching-induced shear strain, allowed by the suppression of 180° polarization switching in our sample. As for the unipolar piezoelectric response, even though the e₁₃* of the 90% Br compound is not larger than that of PMN-PT, the maximum attainable strain is. This is likely due to the high elasticity of the OHF, which makes the sample more resistant to brittle fracture.

To better understand the effect of Br substitution, we carried out ab initio density functional theory (DFT) calculations for (PTMA)CdCl₃ and (PTMA)CdBr₃. Figure 4a shows the minimum energy paths for switching between the two ferroelastic states, illustrating that the energy barrier in the Br compound is greatly reduced with a more flattened double-well landscape compared to the Cl counterpart. It is worth noting that the intermediate state of the ferroelastic switching is featured by mirror-symmetric corner-sharing CdX₄ tetrahedra in which the longest Cd–X bond is broken, reminiscent of the HTP structure. The switching process can be visualized as the bond switching (breaking and reformation) between Cd and the two adjacent apex halide atoms (Supplementary Videos 4 and 5). We then evaluated the bond strength by calculating the crystal orbital Hamilton populations (COHPs) of the longest Cd–X bond, which makes the sample more resistant to brittle fracture.

Our study reveals the great potential of hybrid ferroelectrics in achieving large electromechanical responses. The strategy of structural confinement combined with the diversity of organic molecules make it possible to tailor electromechanical outputs by tactical consideration of the size, symmetry and conformation of the molecules.

**Online content**

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of
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Methods

Synthesis of (PTMA)CdBr$_3$Cl$_{1−x}$ (0 ≤ x ≤ 1) single crystal. All the chemicals were purchased from Sigma-Aldrich and used as received. Single crystals of (PTMA)CdBr$_3$Cl$_{1−x}$ were synthesized by slow evaporation of mixture solutions of filtered acetonitrile and deionized water (acetoniitride:deionized water = 3:2 for 0 ≤ Br concentration ≤ 63%, 4:1 for 63% < Br concentration ≤ 100%) with stoichiometric ratios of PTMA-CI, PTMA-Br, CdCl$_3$ and CdBr$_2$-4H$_2$O. Hexagonal prism shape crystals with centimetre length were obtained upon slow evaporation of the solutions at room temperature for around three weeks. Pure bromide crystals are pale blue in colour. With a higher Cl content, the colour of the crystal becomes lighter. (PTMA)CdBr$_3$Cl$_{1−x}$ with Br percentages of 15%, 29%, 45%, 63%, 70%, 77%, 80% and 90% were obtained using precursors with Br molar percentages of 20%, 33%, 50%, 67%, 73%, 80%, 87% and 96%, respectively. The Br concentration in the crystals was calculated on the basis of the C, H and N mass fractions measured using an elemental analyser (PerkinElmer 2400 Series II).

XRD measurement. Powder XRD patterns were measured using Cu Kα radiation (λ = 1.540598 Å, 40 kV and 30 mA) on a commercial diffractometer (Panalytical Xpert). Single-crystal XRD patterns were collected using a Bruker APEX II diffractometer with a Mo source (λ = 0.71073 Å). The crystal structures were solved using the Bruker SHELLXTL software package and refined for all data using the full-matrix least-squares on F2 method. All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned with appropriate isotropic thermal parameters and included in the structure factor calculations. The data can be obtained free of charge from the Cambridge Crystallography Data Center via a web form (http://www.ccdc.cam.ac.uk/data_request/cif).

DSC and thermogravimetric analyses measurements. Thermal analyses were performed using DSC (TA Instruments Q10) by heating and cooling the crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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Author contributions

Y.H., L.Y., H.J.F. and J.W. conceived the idea and designed the project. Y.H. grew the single crystals and performed the powder XRD measurements. S.A.M. and Y.H. conducted the powder XRD analysis. L.Y. and S.A.M. performed the single-crystal XRD characterization and analysis. Y.H. prepared the devices and carried out the DFT, ferroelectric, piezoelectric, dielectric, and PFM measurements and analyzed the results with L.Y., J.W. and H.J.F. Y.H., L.Y. and P.S.L. conducted the shear strain characterizations. B.X., Y.Z. and X.W. carried out the DFT calculations. Y.H., L.Y., H.J.F. and J.W. wrote the manuscript with input from all the authors.

Competing interests

The authors declare no competing interests.

Additional information

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