Improper molecular ferroelectrics with simultaneous ultrahigh pyroelectricity and figures of merit

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Although ferroelectric materials exhibit large pyroelectric coefficients, their pyroelectric figures of merit (FOMs) are severely limited by their high dielectric constants because of the inverse relationship between FOMs and dielectric constant. Here, we report the molecular ferroelectric [Hdabco]ClO4 and [Hdabco]BF4 (dabco = diazabicyclo[2.2.2]octane) exhibiting improper ferroelectric behavior and pyroelectric FOMs outperforming the current ferroelectrics. Concurrently, the improper molecular ferroelectrics have pyroelectric coefficients that are more than one order of magnitude greater than the state-of-the-art pyroelectric Pb(Mg1/3Nb2/3)O3-PbTiO3. Our first-principles and thermodynamic calculations show that the strong coupling between the order parameters, i.e., the rotation angle of anions and polarization, is responsible for the colossal pyroelectric coefficient of the molecular ferroelectrics. Along with the facile preparation and self-poling features, the improper molecular ferroelectrics hold great promise for high-performance pyroelectric devices.

INTRODUCTION

The pyroelectric effect refers to the polarization change of polar materials in response to the variation in temperature and is used in a wide variety of applications ranging from infrared (IR) detection to thermal imaging and energy harvesting (1, 2). The typical pyroelectric materials are ferroelectric single crystals, ceramics, and polymers, such as triglycine sulfate (TGS), lithium tautalate (LiTaO3), lead zirconate titanate [PbZrTiO3 (PZT)], lead magnesium niobate lead titanate [Pb(Mg1/3Nb2/3)O3-PbTiO3 (PMN-PT)], and poly(vinylidene fluoride) (PVDF), which have large pyroelectric coefficients (p) arising from the variation of their spontaneous polarization (P0) with temperature (T), i.e., |∂P0/∂T| (1, 3–5).

Several figures of merit (FOMs) have been formulated for pyroelectric materials to evaluate their relative potentials for a number of different applications. For example, for pyroelectric sensors, the FOMs are voltage responsivity FR = p/(ε0εrεV) and detectivity FD = p/[(ε0εrεVtanδ)1/2], where ε0, εr, and VT are the vacuum permittivity, dielectric constant, volumetric heat capacity, and loss tangent, respectively (1, 6). FD denotes the maximum pyroelectric voltage for a given energy input, while FR characterizes the ability of detectors to sense weak signals that compete with noises. For pyroelectric energy harvesting, the FOMs are FE = p2/[(ε0εrεV)] and EN = FR = p2VT/(ε0εrεV) (also termed as the electrothermal coupling factor k2, where T0 is the maximum temperature in the thermal cycle), which represent the amount and efficiency of electric power converted from a given thermal energy input, respectively (1, 6–8). Therefore, to achieve high pyroelectric FOMs and factors, it necessitates that pyroelectric materials have simultaneously a high pyroelectric coefficient and a low dielectric constant.

To improve the pyroelectric FOMs, existing approaches have mainly been focused on the structural modification of ferroelectric materials to attain high pyroelectric coefficients (1). For example, by varying the PbTiO3 content, the pyroelectric coefficient of PMN-PT reaches the maximum value of 3000 to 5000 μC m−2 K−1 near the rhombohedral-tetragonal phase transition (4). The addition of 15% Sr into Ba0.85Ca0.15Zr0.1Ti0.9O3 (BCZT) ceramic increases the polarization from 16 to 25 μC cm−2 and, consequently, the pyroelectric coefficient from 700 to 1400 μC m−2 K−1 (9). However, the improvement in the pyroelectric coefficient of ferroelectric materials is generally accompanied by an increase in the dielectric constant (note S1), thus imposing a fundamental limit on the magnitude of the pyroelectric FOMs (10).

The unique characteristics of improper ferroelectricity offer the potential for overcoming this fundamental limitation (11). Contrary to proper ferroelectric whose primary order parameter is polarization, the polarization of improper ferroelectric is a secondary order parameter that develops following the primary order parameter (12–14). In improper ferroelectrics, the dielectric constant remains low even close to the phase transition temperature, which is usually more than one to two orders of magnitude lower than those of proper ones (4, 9, 15). The low dielectric constant of improper ferroelectrics is thus conducive to large pyroelectric FOMs. Relatively high pyroelectric FOMs have been demonstrated in improper ferroelectric dicalcium-lead-propionate [Ca2Pb(CH3CH2COO)2] (DLP) and iron-iodine-boracite [FeB2O3:1:1 (TMO)] stemming from their relatively low dielectric constant of 4 to 13 (16). A favorable electrothermal coupling factor has been revealed in stuffed aluminate sodalite [(Ca0.45Sr0.06)2Al2O7]2:1:1 (MOO4)2, CSAM-16) for thermal energy harvesting (7, 17). Nevertheless, the pyroelectric coefficients of DLP and TMO, for example, are ~60 and ~80 μC m−2 K−1, respectively, which are vastly inferior to those of PMN-PT (3000 to 5000 μC m−2 K−1) and PZT (210 μC m−2 K−1) (4, 18). This is likely due to the nature of second-order phase transitions in these improper ferroelectrics, in

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which the polarization decreases slowly with an increasing temperature around the phase transition temperature. The improper ferroelectric di-\textit{n}-butylanilinium trifluoroacetate, which exhibits a first-order phase transition, presents a large pyroelectric coefficient of 5500 \textmu C m\textsuperscript{-2} K\textsuperscript{-1} and high FOMs of $F_\text{V} = 0.58$ m\textsuperscript{2} C\textsuperscript{-1} and $F_\text{D} = 1.5 \times 10^{-5}$ Pa\textsuperscript{-1/2} (19).

Here, we report improper molecular ferroelectric [Hdabco]ClO\textsubscript{4} and [Hdabco]BF\textsubscript{4} (dabco = diazabicyclo[2.2.2]octane) that have far superior pyroelectric coefficients and FOMs to the current ferroelectric materials. Our first-principles and thermodynamic calculations reveal the decisive role of the coupling between the rotation of [ClO\textsubscript{4}]\textsuperscript{-} anion, the primary order parameter of the improper phase transition, and the polarization, the secondary order parameter, in the pyroelectric responses of the molecular ferroelectrics. Moreover, different from conventional ferroelectrics, [Hdabco]ClO\textsubscript{4} is capable of operating cyclically at the ferroelectric-paraelectric phase transition temperature, i.e., the Curie temperature ($T_\text{C}$), without visible signs of degradation in the pyroelectric coefficient.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) was performed on [Hdabco]ClO\textsubscript{4} to reveal its atomic structures in orthorhombic and tetragonal phases (Fig. 1, fig. S1, and table S1). The crystal structures of [Hdabco]ClO\textsubscript{4} are illustrated in Fig. 1 (C to F). At 303 K, the appearance of the (020), (200), (111) diffraction peaks at $2\theta = 18.40^\circ$, 19.96$^\circ$, and 21.34$^\circ$, respectively (Fig. 1A), manifests the orthorhombic phase of ferroelectric [Hdabco]ClO\textsubscript{4} adopting the noncentrosymmetry $Pn2_1n$ space group (Fig. 1, C and E). The lattice parameters of [Hdabco]ClO\textsubscript{4} extracted from the XRD pattern are $a = 8.827$ Å, $b = 9.714$ Å, and $c = 5.378$ Å. With the increase of temperature, e.g., at 403 K, [Hdabco]ClO\textsubscript{4} is highly disordered and exhibits a tetragonal structure assigned to the centrosymmetric $P4/mnm$ space group (Fig. 1, D and F) with lattice parameters of $a = b = 6.672$ Å and $c = 5.369$ Å (Fig. 1B and fig. S1). Second-harmonic generation (SHG) was performed to provide further insight into the local symmetry (19, 20). As shown in Fig. S2, at temperatures above 378 K, which is the $T_\text{C}$ of [Hdabco]ClO\textsubscript{4} determined from dielectric spectroscopy (Fig. 2A), the SHG signal is close to zero, reaffirming the centrosymmetric phase structure of [Hdabco]ClO\textsubscript{4}. The symmetry of [Hdabco]ClO\textsubscript{4} is broken as temperature decreases to below 378 K as evidenced by the emergence of the SHG signals (20). The differential scanning calorimetry (DSC) profile measured at a heating and cooling scan rate of 1 K min$^{-1}$ shows distinct endothermic and exothermic peaks with a heat hysteresis of 3 K (fig. S3A), which is a clear manifestation of the first-order phase transition (21). The heat hysteresis grows more pronounced by increasing the rate of heating and cooling (fig. S3B).

Figure 2A presents the dielectric spectra of [Hdabco]ClO\textsubscript{4} as a function of temperature, in which the dielectric constant step corresponding to the ferroelectric-paraelectric phase transition appears at 378 K. [Hdabco]ClO\textsubscript{4} shows a bistable dielectric constant spanning the ferroelectric and paraelectric phases with relative permittivities of 9 and 18, respectively, measured at 1 kHz, which is distinctly different from proper ferroelectrics with a dielectric constant peak obeying the Curie-Weiss law around the Curie temperature (22–24). Meanwhile, [Hdabco]ClO\textsubscript{4} has a loss tangent of 0.001 before the $T_\text{C}$ and 0.08, which is comparable to that of PZT thin films (18), after the $T_\text{C}$ (Fig. 2A).

The polarization-field ($P$-$E$) loops of [Hdabco]ClO\textsubscript{4} were recorded to evaluate its ferroelectricity. As shown in Fig. 2B and fig. S4, at ambient temperature, a saturated ferroelectric hysteresis loop with a polarization of ~6 \textmu C cm$^{-2}$ and a coercive field of 75 kV cm$^{-1}$ is attained using the Sawyer-Tower circuit. The ferroelectric nature of [Hdabco]ClO\textsubscript{4} is further confirmed by the current–electric field ($I$-$E$) curve. As shown in Fig. S4, the current is maximized exactly at the coercive field instead of the maximum electric field, which is known as a direct evidence of ferroelectricity as the current peak is generated by the dipole reversal rather than electrical conductivity. The $P$-$E$ loops of [Hdabco]ClO\textsubscript{4} at different temperatures are shown in Fig. 2B. The minor change of the $P$-$E$ loops measured at temperatures below 378 K indicates the ferroelectric stability of orthorhombic [Hdabco]ClO\textsubscript{4}. When the temperature exceeds 378 K, the near-square hysteresis loops are transformed into slim linear loops, accompanied by a dramatic decrease in polarization, owing to the formation of the paraelectric phase. As indicated by the light blue area in Fig. 2C, the spontaneous polarization of [Hdabco]ClO\textsubscript{4} shows an abrupt change to nearly zero around the $T_\text{C}$, suggesting an extremely high $dP/dT$ and a giant pyroelectric coefficient of [Hdabco]ClO\textsubscript{4}.

The pyroelectric measurements were carried out using the Byer-Roundy method. The maximum pyroelectric coefficient of 48,000 \textmu C m$^{-2}$ K$^{-1}$ is achieved in [Hdabco]ClO\textsubscript{4} at the $T_\text{C}$ of 378 K (Fig. 2D), which far exceeds the state-of-the-art pyroelectric materials,
e.g., about 16 and 50 times greater than the typical proper pyroelectric materials such as PMN-PT and barium zirconate titanate (BZT), respectively, more than three orders of magnitude higher than those of ferroelectric polymers, and 8 times larger than the newly developed improper dielectric di-n-butylaminium trifluoroacetate (Fig. 3 and Table 1) (1, 4, 9, 19). Notably, as shown in Fig. 3, the colossal pyroelectric coefficient of [Hdabco]ClO$_4$ is coupled with a dielectric constant that is orders of magnitude lower than those of PMN-0.13PT (>3100) and PZT (>375). This is in stark contrast to the existing pyroelectric materials showing the positive relationship between the pyroelectric coefficient and the dielectric constant (10).

Consequently, [Hdabco]ClO$_4$ exhibits the state-of-the-art FOMs, i.e., $F_V$ of 5.58 m$^2$ C$^{-1}$, $F_D$ of 25.2 $\times$ 10$^{-5}$ Pa$^{-1/2}$, $F_E$ of 1.36 $\times$ 10$^7$ J m$^{-3}$ K$^{-2}$, and $F_{EN}$ of 20.6% around $T_C$ (Fig. 2, E to G, and Table 1), far outperforming the current proper and improper ferroelectrics as compared in Table 1. At room temperature, although the pyroelectric coefficients of [Hdabco]ClO$_4$ and [Hdabco]BF$_4$ are inferior to those of most proper ferroelectrics, the FOMs of these two improper ferroelectrics are still comparable to those of proper ferroelectrics because of their small and stable dielectric constants.

The process of poling using a sufficiently large electric field is required for traditional ferroelectric materials to align the electric dipoles for macroscopic pyroelectric responses. In contrast, high pyroelectric signals in [Hdabco]ClO$_4$ are obtained without poling due to the spontaneous formation of the orientated polarization during the growth of [Hdabco]ClO$_4$, which is validated by piezoresponse force microscopy (PFM). Figure S5 presents the domain orientations at four random places of a fresh [Hdabco]ClO$_4$ film. It is seen that all the domains direct toward the same direction, indicating that the dipoles spontaneously align along the same direction during the deposition process. The self-poling field estimated from the $P$-$E$ loops is $\sim$12 kV cm$^{-1}$, which is about 20% of the coercive field (Fig. S6). Because of the self-poling effect, when operating cyclically across the $T_C$, no obvious decay in the pyroelectric coefficient was observed in [Hdabco]ClO$_4$, as shown in fig. S7. On the contrary, most conventional ferroelectric materials lose their pyroelectric activity at temperatures above the $T_C$ and are unable to regain pyroelectricity even after the temperature drops below the $T_C$ unless they are repoled under an applied electric field. The self-poling effect can be counteracted by applying a reversed electric field whose magnitude is equal to the coercive field with the self-poling effect ($E_C^2$ in fig. S6A). As shown in fig. S6B, the offset of the $P$-$E$ loop decreases notably after poling with the reversed field. The pyroelectric response of the sample poled with the reversed field is only about one-eighth those of the unpoled specimen (fig. S8).

**Fig. 2.** The dielectric, ferroelectric, and pyroelectric properties of [Hdabco]ClO$_4$. (A) Dielectric constant ($\varepsilon_r$) and loss tangent (tan$\delta$) of [Hdabco]ClO$_4$ as a function of temperature. (B) Polarization-field ($P$-$E$) loops of [Hdabco]ClO$_4$ measured at 100 Hz and different temperatures. (C) Spontaneous polarization ($P_S$) as a function of temperature. A marked drop is observed at 378 K, corresponding to the Curie phase transition. (D) Temperature-dependent pyroelectric coefficient ($\rho$). (E) Voltage responsivity ($F_V$). (F) Detectivity ($F_D$). (G) FOM of energy harvesting ($F_{EN}$).
To understand the experimental results of [Hdabco]ClO$_4$, we calculated the static dielectric constant ($\varepsilon_{\text{std}}$), including the electronic ($\varepsilon_{\text{elec}}$) and ionic ($\varepsilon_{\text{ion}}$) contributions, and Born effective charges ($Z^*$) using the first-principles method, and the results are summarized in tables S2 and S3. The calculated $\varepsilon_{\text{std}}$ of [Hdabco]ClO$_4$ are $\varepsilon_{\text{elec}}^{\text{std}} = 7.76$, $\varepsilon_{\text{ion}}^{\text{std}} = 3.35$, and $\varepsilon_{\text{tot}}^{\text{std}} = 4.05$, which are comparable to the experimental values at room temperature (Fig. 2A). For the purpose of comparison, the corresponding theoretical values of a typical organic-inorganic ferroelectric materials. The units of temperature, $p$, $c_v$, $F_D$, and $F_{\text{EN}}$ are K, μC m$^{-3}$ K$^{-1}$, MJ m$^{-3}$ K$^{-1}$, m$^2$ C$^{-1}$, 10$^{-5}$ Pa, J m$^{-3}$ K$^{-1}$, and %, respectively. RT, room temperature.

| Materials | Temperature | $p$ | $c_v$ | $\varepsilon_r$ | $\tan\delta$ | $F_{\text{V}}$ | $F_D$ | $F_E$ | $F_{\text{EN}}$ | References |
|-----------|-------------|-----|-------|---------------|-------------|------------|--------|--------|--------------|------------|
| PbZrO$_3$ | –RT         | 400 | 2.5   | 290           | 0.003       | 0.062      | 5.8    | 62.3   | 0.74         | (15)       |
|           | –T$_C$      |     |       |               |             |            |        |        |              |            |
| PbTiO$_3$ | –RT         | 350 | 2.2   | 220           | 0.001       | 0.082      | 11.4   | 62.9   | 0.85         | (15, 48)   |
|           | –T$_C$      |     |       |               |             |            |        |        |              |            |
| Pb(Zr,Ti)O$_3$ | –RT | 211 | 3.15  | 365           | 0.089       | 0.021      | 0.4    | 13.8   | 0.13         | (18)       |
|           | –T$_C$      |     |       |               |             |            |        |        |              |            |
| 0.7Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-0.3PbTiO$_3$ | –RT | 1,200 | 2.7      | 1800           | 0.04        | 0.028      | 3.5    | 90.4   | 1            | (4, 49, 50) |
|           | –T$_C$      | 3,000 | – | 17,000 | 0.08       | 0.007      | 1      | 59.8   | –            |            |
| LiTaO$_3$ | –RT         | 230 | 0.75  | 55            | 0.03        | 0.630      | –      | 108.6  | 4.4          | (5, 51)    |
|           | –T$_C$      | 9,800 | 1.02    | 2600           | –           | –          | –      | 4172   | –            |            |
| LiNbO$_3$ | –RT         | 83  | 2.32  | 28            | 0.04        | 0.144      | –      | 27.8   | 0.4          | (2, 52)    |
| Sr$_0.5$Ba$_0.5$Nb$_2$O$_6$ | –RT | 550 | 2.34  | 400           | 0.003       | 0.066      | 7.2    | 85.4   | 1.1          | (45, 53, 54) |
| 94.6Na$_0.5$Bi$_0.5$TiO$_3$-5.48BaTiO$_3$ | –RT | 588 | 2.89  | 279           | 0.019       | 0.082      | 3      | 140    | 1.4          | (55, 56)   |
| BaCe$_{0.12}$Ti$_{0.88}$O$_3$ | –RT | 381 | 2.09  | 4117          | 0.055       | 0.005      | 0.4    | 4      | 0.06         | (46, 57)   |
|           | –T$_C$      | 8,900 | 0       | 13,300       | 0.014       | 0.036      | 10.5   | 672.7  | –            |            |
| Ba$_{0.85}$Ca$_{0.15}$Zr$_{0.1}$Ti$_{0.9}$O$_3$ | –RT | 700 | 2.33  | 2743          | 0.023       | 0.012      | 1.3    | 20.2   | 0.26         | (9, 58)    |
|           | –T$_C$      | 980  | –       | 5500          | 0.059       | 0.009      | 0.79   | 19.7   | –            |            |
| Triglycinesulfate (TGS) | –RT | 400 | 2.6   | 38            | 0.018       | 0.457      | 6.25   | 475.6  | 5.5          | (3)        |
|           | –T$_C$      | 550  | –       | 55            | 0.025       | 0.434      | 6.06   | 621.2  | –            |            |
| Deuterated triglycinesulfate (DTGS) | –RT | 350 | 2.4   | 31            | 0.018       | 0.531      | 6.65   | 446.3  | 5.64         | (3)        |
|           | –T$_C$      | 550  | –       | 43            | 0.02        | 0.602      | 8.31   | 794.5  | –            |            |
| PVDF      | –RT         | 12  | 2.6   | 8             | 0.03        | 0.065      | 0.35   | 2.03   | 0.023        | (1)        |
|           | –T$_C$      |     |       |               |             |            |        |        |              |            |
| P(VDF/TrFE) | –RT | 52  | 2.2   | 18            | 0.053       | 0.148      | 0.81   | 16.97  | 0.23         | (47, 59)   |
|           | –T$_C$      | 142 | 2.2   | 33            | 0.04        | 0.221      | 1.89   | 69.01  | 1.03         |            |
| Ca$_3$Pb(CH$_3$CH$_2$COO)$_6$ (DLP) | –RT | 60  | –     | 8              | 0.54        | –          | 50.8   |        |              | (16)       |
|           | –T$_C$      |     |       |               |             |            |        |        |              |            |
| Fe$_3$O$_3$ (TM0) | –RT | 80  | –     | 13             | 0.58        | –          | 55.6   |        |              | (16)       |
| Di-n-butylammonium trifluoracetate | –RT | 5,500 | –   | 9.3           | 0.018       | 0.58       | –      | 3.7×10$^5$ |              | (19)       |
| (Ca$_{0.84}$Sr$_{0.16}$)(AlO$_2$)$_2$ (MoO$_2$)$_2$ | –RT | 1   | 2.78  | 9.7           | 0.01        | 0.004      | 0.04   | 0.012  | 1.2×10$^{-4}$ | (7)        |
|           | –T$_C$      | 120 | –     | 12.4          | 0.03        | 0.39       | 2.38   | 131.16 | 2.09         |            |
| [Hdabco]ClO$_4$ | –RT | 83  | 1.23  | 8.7           | 0.005       | 0.88       | 10.9   | 89.43  | 2.2          |            |
|           | –T$_C$      | 48,000 | 51.8  | 18.4         | 0.08        | 5.58       | 25.2   | 1.36×10$^7$ | 20.6        |            |
| [Hdabco]BF$_4$ | –RT | 81  | 2.14  | 16.5          | 0.003       | 0.26       | 5.7    | 44.91  | 0.63         |            |
|           | –T$_C$      | 38,200 | 18.1 | 38.5         | 0.09        | 6.19       | 38.1   | 2.73×10$^6$ | 59.9        | This work  |
compound CH$_3$NH$_3$PbI$_3$ were computed (table S3). [Hdabco]ClO$_4$ only contains light elements (Cl and O), leading to its higher IR-active phonon mode frequencies ($\omega_n$) than those of CH$_3$NH$_3$PbI$_3$ with heavier elements (Pb and I). As $\varepsilon_{\text{pol}}$ is inversely proportional to the frequency of the $\lambda_{\text{th}}^n \omega_n$ ($25$), $\varepsilon_{\text{pol}}$ of [Hdabco]ClO$_4$ is smaller than that of CH$_3$NH$_3$PbI$_3$. Because the ionic part contributes mostly to the $\varepsilon_{\text{el}}$, the small $\varepsilon_{\text{pol}}$ is responsible for the lower $\varepsilon_{\text{tot}}$ of [Hdabco]ClO$_4$ compared to CH$_3$NH$_3$PbI$_3$ ($26$). Along with a relatively small $Z^*$ (table S2), [Hdabco]ClO$_4$ therefore has a low dielectric constant.

We performed the first-principles calculations and thermodynamics simulations to unveil the origin of the ultrahigh pyroelectric coefficient found in [Hdabco]ClO$_4$. The comparison of the polar and nonpolar structures of [Hdabco]ClO$_4$ reveals two apparent differences: the rotation of [ClO$_4$]$^-$ ($\theta$; Fig. 1C) and the columnar shift (polarization) of the centers of [Hdabco]$^+$ and [ClO$_4$]$^-$ groups along the $b$ direction ($\delta$; Fig. 1E). We then chose $\theta$ as the primary order parameter and $\delta$ as the secondary parameter corresponding to polarization in the Landau-Devonshire theory, which is also in line with the coupling scheme of different distortions to induce improper ferroelectricity in molecular materials ($27$–$29$). The rotation of [ClO$_4$]$^-$ versus energy was calculated to provide the fitting parameters for thermodynamics analysis using the Landau-Devonshire theory based on the spontaneous polarization-temperature ($P_s$-$T$) curves from our experimental results. The general formula of free energy for improper ferroelectrics is given by $G = \alpha_1 \theta^2 + \alpha_2 \theta + \beta_1 \theta^2 + \gamma_1 \theta^2 P^2 + \gamma_2 \theta^2 P^2$ ($30$–$32$), where $\alpha_1$, $\alpha_2$, $\beta_1$, and $\beta_1$ are the Landau coefficients; $\theta$ is the primary order parameter; $P$ is the polarization; $\gamma_1$, $\gamma_2$, $P^2$, and $\theta^2 P^2$ are respectively the linear and nonlinear coupling between $\theta$ and $P$ in terms of polarization; and $\gamma_1$ and $\gamma_2$ represent the coupling coefficients, respectively. The values of Landau and coupling coefficients are summarized in table S4. It is found from the thermodynamic calculation that the $P_s$ decreases significantly from ~5 $\mu$C cm$^{-2}$ to zero and shows the first-order transition near the $T_C$ (Fig. 4A).

The calculated $P_s$-$T$ curve is in good agreement with the experimental result, which verifies our calculations. The calculated pyroelectric coefficient of about 46,700 $\mu$C cm$^{-2}$ K$^{-1}$ (table S5) also agrees well with the experimental result.

For comparison, we prepared and characterized [Hdabco]BF$_4$ with the same lattice structure as [Hdabco]ClO$_4$ ($20$), which also shows a bistable dielectric behavior at the Curie transition (fig. S7B). The pyroelectric coefficient of [Hdabco]BF$_4$ measured by the Byer-Roundy method is 38,200 $\mu$C m$^{-2}$ K$^{-1}$, which is less than that of [Hdabco]ClO$_4$ (fig. S7D). We calculated the $P_s$-$T$ curve of [Hdabco]BF$_4$ (Fig. 4A) using the same thermodynamic scheme performed on [Hdabco]ClO$_4$, and the calculated pyroelectric coefficient is 37,600 $\mu$C m$^{-2}$ K$^{-1}$ (table S5).

The high pyroelectric coefficients of [Hdabco]ClO$_4$ and [Hdabco]BF$_4$ are obtained because the temperature dependence of polarization is dominated by the primary order parameter $\theta$ in improper ferroelectrics. As exhibited in Fig. 4B, according to the thermodynamic calculation, it can be seen that the $P_s$ is strongly dependent on the primary order parameter $\theta$ ($21$, $33$). As the $\theta$ for the materials is a function of temperature, the pyroelectric coefficient of the improper ferroelectrics is determined by the coupling effect between the primary order parameter and the polarization. As listed in table S5, a larger slope of the $P$-$\theta$ curve of [Hdabco]ClO$_4$ thus results in a higher pyroelectric coefficient in comparison to [Hdabco]BF$_4$. Therefore, the high pyroelectric coefficients of [Hdabco]ClO$_4$ and [Hdabco]BF$_4$ are attributable to the strong coupling effect between the primary order parameter $\theta$ and the secondary order parameter $\delta$.

Compared to the proper ferroelectric, improper ferroelectric remains largely unexplored for technological applications, although their structures and properties are of significant fundamental scientific importance. In this work, we demonstrate an efficient route to overcoming the fundamental limitation of proper ferroelectrics and significant improvement of the pyroelectric FOMs by capitalizing on the unique features of improper ferroelectric. The exceptional combination of an ultrahigh pyroelectric constant and a low dielectric constant in the improper molecular ferroelectric addresses the “high pyroelectric coefficient associated with large dielectric constant” dilemma in the current ferroelectric materials, providing a new degree of freedom in the design of pyroelectric materials that is not accessible to proper ferroelectrics. We observe unprecedentedly large pyroelectric coefficient and the pyroelectric FOMs from improper molecular ferroelectric [Hdabco]ClO$_4$ and [Hdabco]BF$_4$. We explain the observed dielectric and pyroelectric behavior using first-principles calculations and thermodynamics simulations and reveal the impact of the coupling of the primary order parameter and the secondary order parameter on the pyroelectric coefficient of the improper molecular ferroelectric. Moreover, our materials are found to retain their high pyroelectric responses when operating cyclically across the $T_C$. The unexpectedly high pyroelectric performance and unconventional mechanisms of improper ferroelectrics may provide...
a new paradigm for applying molecular design guidelines to fundamentally enable their technological applications. The high pyroelectric coefficients reported herein are observed in a relatively narrow temperature range near the Curie transition (Fig. 2 and figs. S9 and S10) because of the first-order phase transition nature. Achieving high pyroelectric coefficients in a wide temperature range represents a critical direction for future research in the field. It is anticipated that the significant breakthrough can be realized in the molecular ferroelectrics given their design flexibility and structure tunability (34, 35).

MATERIALS AND METHODS

Sample preparation

All reagents and solvents were commercial and implemented without further purification. 1,4-Diazabiclooctane triethylenediamine (Dabco) (98%, Aladdin) and perchloric acid (HClO₄) (analytically pure, Sinopharm Chemical Reagent) were dissolved in deionized water with a ratio of 1:1 and stirred for 30 min. [Hdabco]ClO₄ was precipitated out with the slow evaporation of the solution. The collected [Hdabco]ClO₄ powder was then dissolved in deionized water to form a clear solution (100 mg ml⁻¹). Subsequently, the solution was cast onto an indium tin oxide glass, and a layer of [Hdabco]ClO₄ film was deposited on the substrate after solvent evaporation. The [Hdabco]BF₄ crystal was synthesized with equimolar dabco and fluoboric acid (HBF₄). The synthesis process is the same as that of [Hdabco]ClO₄.

Sample characterization

The information of phase and crystalline structure was analyzed at different temperatures by an XRD with a Cu Kα radiation (Empyrean, PANalytical B.V., The Netherlands). DSC was conducted by using a DSC-204F1 differential scanning calorimeter (TA Instrument Co., DE, USA). PFM was performed with a Smeina P47HD (NT-MDT Co., Moscow, Russia). SHG measurement was carried out to explore the nonlinear optical property of the materials. The incident laser is produced by a Ti:sapphire oscillator with a central wavelength of 800 nm, a pulse duration of 120 fs, and a repetition of 82 MHz. Au top electrodes with a diameter of 1 mm were sputtered by an ion sputter coater (SBC-12, KYKY, China) for the electrical measurements. The reciprocal susceptibility can be given by

\[
\chi = \frac{1}{\varepsilon_0} = \frac{1}{\varepsilon_0} = \frac{(\partial^2 G)}{(\partial P^2)}_{P=P_c} = 2 \beta_1 + 2 \gamma_2 \theta^2 P \quad (6)
\]

where \( P = \frac{\partial P}{\partial T} \)

The reciprocal susceptibility can be given by

\[
\frac{P}{\varepsilon} = \frac{4 \alpha_0 \theta (\beta_1 + \gamma_2 \theta^2)}{\gamma_1 + 4 \gamma_2 \theta P} \quad (7)
\]

At a steady state, the variation of energy with order parameters was taken to be zero; therefore, \( \frac{\partial G}{\partial P} = 0 \) and \( \frac{\partial G}{\partial \theta} = 0 \), and we had

\[
0 = 2 \beta_1 P + \gamma_1 \theta + 2 \gamma_2 \theta^2 P \quad (8)
\]

\[
0 = 2 \alpha_0 \theta + 4 \alpha_{11} \theta^3 + 6 \alpha_{111} \theta^5 + \gamma_1 P + 2 \gamma_2 \theta P^2 \quad (9)
\]

Combining the above two equations and eliminating the primary order parameter \( \theta \), we got

\[
\gamma_1 \theta_1 \rightleftharpoons \frac{4 \alpha_0 \theta (\beta_1 + \gamma_2 \theta^2)}{\gamma_1 + 4 \gamma_2 \theta P} \quad (10)
\]
Experimental $P_S-T$ data were fitted on the above equation to derive the values of the coefficients $a_0$, $a_1$, $a_{11}$, $b_1$, $y_1$, and $y_2$ with the assumption that $a_0$ and $a_11$ depend on environmental factors/experimental conditions. $a_{11}$ is considered to be temperature dependent, and low-temperature quantum effects were incorporated in $a_1$ and $a_{11}$ in the calculation (43). Therefore, at temperatures above $T_C$, $a_{11}$ is given as

$$a_{11} = a_{11}(T)$$  \hspace{1cm} (11)

whereas at temperatures below $T_C$, $a_1$ and $a_{11}$ take the form

$$a_1 = a_0 T_c \left( \frac{T}{T_c} \right) \coth \left( \frac{T}{T_c} \right) - \coth \left( \frac{T}{T_c} \right)$$  \hspace{1cm} (12)

$$a_{11} = b_{11} T_c \left( \frac{T}{T_c} \right) \coth \left( \frac{T}{T_c} \right) - \coth \left( \frac{T}{T_c} \right)$$  \hspace{1cm} (13)

where $T_C$ is the saturated temperature below which quantum effects become significant; here, we used $T_c$ taken experimentally from KH$_2$PO$_4$ crystal with similar disorder phase transition (44). The extracted coefficients are listed in table S4.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/7/5/eabe3068/DC1

**REFERENCES AND NOTES**

1. R. W. Whatmore, Pyroelectric devices and materials. *Rep. Prog. Phys.* **49**, 1335–1386 (1986).

2. S. B. Lang, Pyroelectricity: From ancient curiosity to modern imaging tool. *Phys. Today* **58**, 31–36 (2005).

3. P. Felix, P. Gamot, P. Lacheau, Y. Raverdy, Pyroelectric, dielectric and thermal properties of TGS, DTGS and TGFb. *Ferroelectrics* **17**, 543–551 (1977).

4. J. H. Park, B. K. Kim, K. H. Song, S. J. Park, Electric-field induced strains and pyroelectric coefficients in lead magnesium niobate-lead titanate solid solutions. *Mater. Res. Bull.* **30**, 435–441 (1995).

5. B. M. Kulwicki, A. Amin, H. R. Beratan, C. M. Hanson, Pyroelectric imaging. *Proc. IEEE Int. Symp. Appl. Ferroelectrics*, 1–10 (1992).

6. S. B. Lang, D. K. Das-Gupta, Chapter 1—Pyroelectricity: Fundamentals and applications, in Handbook of Advanced Electronic and Photonic Materials and Devices (Academic Press, 2001), vol. 4, pp. 1–55.

7. T. Wakamatsu, T. Tanabe, I. Terasaki, H. Taniguchi, Improper ferroelectrics as high-efficiency energy conversion materials. *Phys. Status Solidi RRL* **11**, 1770324 (2017).

8. G. Sebald, E. Lefeuvre, D. Guyomar, Pyroelectric energy conversion: Optimization principles. *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **55**, 538–551 (2008).

9. S. Patel, A. Chauhan, R. Vahash, Large pyroelectric figure of merits for Sr-modified Ba$_2$Zr$_2$O$_7$ ceramics. *Solid State Sci.* **52**, 10–18 (2016).

10. S. T. Liu, J. D. Zook, D. Long, Relationships between pyroelectric and ferroelectric parameters. *Ferroelectrics* **9**, 39–43 (1975).

11. M. E. Lines, A. M. Glass, Principles and Applications of Ferroelectrics and Related Materials (Clarendon Press, 1977).

12. E. Bouquet, M. Dawber, N. Stucki, C. Lichtensteiger, P. Hermet, S. Gariglio, J.-M. Triscone, P. Ghosez, Improper ferroelectricity in perovskite oxide artificial superlattices. *Nature* **452**, 732–736 (2008).

13. N. A. Benedek, C. J. Fennie, Hybrid improper ferroelectricity: A mechanism for controllable polarization-magnetization coupling. *Phys. Rev. Lett.* **106**, 107204 (2011).

14. Y. S. Oh, X. Luo, F.-T. Huang, Y. Wang, S.-W. Cheong, Experimental demonstration of hybrid improper ferroelectricity and the presence of abundant charged walls in (Ca,Sr)$_2$Ti$_2$O$_7$ crystals. *Nat. Mater.* **14**, 407–413 (2015).

15. D. Luff, R. Lane, K. R. Brown, H. J. Marshallay, Ferroelectric ceramics with high pyroelectric properties. *Trans. J. Br. Ceram. Soc.* **73**, 251–264 (1974).

16. A. Shao, W. A. Smith, G. M. Loaiciga, M. I. Bell, Y. H. Tsu, Improper ferroelectrics for pyroelectric detection of infrared radiation. *Ferroelectrics* **27**, 117–121 (1980).

17. Y. Maeda, T. Wakamatsu, A. Konishi, H. Moriwake, C. Moriyoshi, Y. Kurowa, K. Tanabe, I. Terasaki, H. Taniguchi, Improper ferroelectricity in stuffed aluminate sodalites for pyroelectric energy harvesting. *Phys. Rev. Appl.* **7**, 034012 (2017).
et al., Sci. Adv. 2021; 7 : eabe3068

et al.

S.-M. J. Jiang, M.-D. Li, W.-H. Li, Y. Li, Z. Chen, Enhanced cooling capacities of ferroelectric materials at morphotropic phase boundaries. Jpn. J. Appl. Phys. Lett. 50, 242902 (2011).

G. B. Kim, J. M. Jung, S. W. Choi, Synthesis and ferroelectric properties of Ni-modified 0.7Pb(Mg1/3Nb2/3)O3-0.3PbTiO3 solid solution system. Jpn. J. Appl. Phys. 38, 5470–5473 (1999).

A. M. Glass, Dielectric, thermal, and pyroelectric properties of ferroelectric LiTaO3. Phys. Rev. B 172, 564–571 (1968).

R. Liu, R. Guo, A. S. Bhalla, L. E. Cross, M. Levy, R. M. Osgood, A. Kumar, H. Bakrhu, Dielectric and pyroelectric properties of crystal ion sliced (CIS) LiNbO3 thin film. Ferroelectrics 248, 45–56 (2000).

B. Jimenez, C. Alemany, J. Mendiola, E. Maurer, Phase transitions in ferroelectric ceramics of the type Sr2Ba1-2xNb2O6. J. Phys. Chem. Solid 46, 1383–1386 (1985).

M. Venet, I. A. Santos, J. A. Eiras, D. Garcia, Potentiality of SBN textured ceramics for pyroelectric applications. Solid State Ion. 177, 589–593 (2006).

R. Sun, J. Wang, F. Wang, T.-F. Feng, Y. Li, Z. Chi, X. Zhao, H. Luo, Pyroelectric properties of Mn-doped 94.6Na0.5Bi0.5TiO3-0.4BaTiO3 lead-free single crystals. J. Appl. Phys. 115, 074101 (2014).

A. M. Balakt, C. P. Shaw, Q. Zhang, The effects of Ba3+ content on depolarization temperature and pyroelectric properties of lead-free 0.94Na0.5Bi0.5TiO3-0.06Ba1-xTi0.5-xO ceramics. J. Mater. Sci. Mater. Electron. 27, 12947–12954 (2016).

S.-M. Zeng, X.-G. Tang, Q.-X. Liu, Y.-P. Jiang, M.-D. Li, W.-H. Li, Z.-H. Tang, Electrocaloric effect and pyroelectric properties in Ce-doped BaCe0.5Ti1-xO3 ceramics. J. Alloy. Compd. 776, 731–739 (2019).

M. Sharma, V. P. Singh, S. Singh, P. Azad, B. Iahi, N. A. Madhar, Porous Ba2Zn5Ti4O12 ceramics for pyroelectric applications. J. Electron. Mater. 47, 4882–4891 (2018).

A. Navid, C. S. Lynch, L. Pilon, Purified and porous poly(vinylidene fluoride-trifluoroethylene) thin films for pyroelectric infrared sensing and energy harvesting. Smart Mater. Struct. 19, 055006 (2010).

L. Jin, F. Li, S. J. Zhang, Decoding the fingerprint of ferroelectric loops: comprehension of the 306 material properties and structures. J. Am. Ceram. Soc. 97, 1–27 (2014).

A. Katrusiak, M. Ratajczak-Sitarz, E. Grech, Stereochernistry and transformations of NH–N hydrogen bonds Part II. Proton stability in the monosalts of 1,4-diazabicyclo[2.2.2]octane. J. Mol. Struct. 474, 135–141 (1999).

A. Katrusiak, Proton dynamics in NH+–N hydrogen bond in the paraelectric structure of 1,4-diazabicyclo[2.2.2]octane perchlorate. J. Mol. Struct. 552, 159–164 (2000).

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