ChemComm

COMMUNICATION

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Cite this: Chem. Commun., 2021, 57, 943

Received 9th November 2020, Accepted 17th December 2020

DOI: 10.1039/d0cc07377f

rsc.li/chemcomm

A multiaxial molecular ferroelectric with record high $T_{\rm C}$ designed by intermolecular interaction modulation[†]

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Through precise and ingenious molecular modification, we successfully obtained a multiaxial ferroelectric, [FEtDabco]Znl₃ (*N*-fluoroethyl-*N'*-Znl₃-1,4-diazabicyclo[2.2.2]octonium), with a record high T_c (540 K) among molecular ferroelectrics, which is promising for application under extreme thermal conditions.

Ferroelectrics have attracted enormous interest owing to their prominent properties, and have been widely used in piezoelectric sensors, data storage, signal processing and nonlinear optical devices.^{1–3} On account of their flexible, lightweight, easily prepared and environmentally friendly features, molecular ferroelectrics have developed rapidly in recent years, and are promising to become a desired succedaneum of conventional ceramic ferroelectrics, like Pb(Zr, Ti)O₃ (PZT) and BaTiO₃ (BTO), in order to address the growing severe environmental and energy issues.^{4–8}

Recently, 'quasi-spherical theory' has been proposed, which is highly efficient for the design of molecular ferroelectrics.⁹ Specifically, some highly symmetric building blocks, like $[(CH_3)_4N]^+$, pyrrolidinium, 1,4-diazabicyclo[2.2.2]octonium (Dabco) and quinuclidine, are applicable for the construction of molecular ferroelectrics by reasonable modification.^{10–16} Accordingly, a large quantity of high performance ferroelectrics have emerged through the methods of methylation, H/F substitution and hydroxylation.¹⁷ However, compared to outstanding inorganic ferroelectrics, numerous molecular ferroelectrics are severely limited in practical application because of unsatisfactory properties, such as relatively low phase transition temperatures and uniaxial features. Therefore, it is imperative and challenging to discover more valuable molecular ferroelectrics to maximize their advantages mentioned above.

Between the remarkable building blocks, Dabco has aroused our interest due to its outstanding structural flexibility, and has been widely applied not only in the construction of molecular ferroelectrics, but also in magnetic materials and metalorganic frameworks (MOFs).¹⁸⁻²³ Inspired by the role of Dabco in MOFs, we used Dabco as a bridge molecule and a zinc atom is coordinated with the nitrogen atom that is not protonated in Dabco. To be specific, starting from the non-ferroelectric [MeDabco]ZnI₃ (N-methyl-N'-ZnI₃-1,4-diazabicyclo[2.2.2] octonium, compound 1), we designed an ultra-high temperature lead-free molecular ferroelectric [FEtDabco]ZnI3 with a low EC through several precise molecular modifications (Scheme 1). Firstly, H/F substitution was performed on 1. However, compound 2 ([FMeDabco]ZnI₃) still crystallizes in the non-polar space group $P2_1/n$ at room-temperature. Considering the tremendous difference between fluoromethyl and triiodide zinc, we selected an ethyl as the substituent to realize the tender balance between each side of Dabco. Disappointingly, compound 3 crystallizes in the D_{2h} point group, which is not one of the 10 polar point groups $(C_1, C_2, C_{1h}, C_{1h})$ C_{2v} , C_4 , C_{4v} , C_3 , C_{3v} , C_6 , and C_{6v}). Since the lattice has undergone a great transition from a monoclinic one in 1 and 2 to an



Scheme 1 Design methods of ferroelectric [FEtDabco]ZnI $_3$ by momentum matching and H/F substitution.



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[†] Electronic supplementary information (ESI) available: The experimental details and characterization. CCDC 1569848, 2013917–2013919. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0cc07377f

orthorhombic one, we supposed that the H/F substitution would induce the crystallization of a polar point group with a lower symmetry. As excepted, a subtle symmetry break from D_{2h} to C_{2v} was realized successfully and [FEtDabco]ZnI₃ (compound 4) adopts a polar space group *Pna2*₁ at room-temperature. Compound 4 undergoes a 4/*mmmFmm2* type phase transition with a Curie temperature (T_c) of 540 K. To the best of our knowledge, such a high T_c is the highest among previously reported molecular ferroelectrics (Table S1, ESI†). We believe that the molecular modification strategy is promising for the enrichment of high performance ferroelectrics based on similar building blocks.

Colourless bulk crystals of 1-4 were easily obtained by the slow evaporation of aqueous solution. (The specific synthesis methods can be found in the ESI.[†]) The phase purity of 4 was confirmed by infrared spectrum (IR) and powder X-ray diffraction (PXRD) measurements (Fig. S1 and S2, ESI⁺). The thermogravimetric analysis (Fig. S3, ESI⁺) demonstrates outstanding thermostability of 4, which is stable below 576 K. The phase transition behaviour was firstly investigated by differential scanning calorimetry (DSC) measurement from roomtemperature to 570 K. As shown in Fig. 1, a distinct thermal anomaly was observed at around 540 K, indicating that a phase transition occurred at an extremely high temperature (Fig. S4, ESI[†]). The entropy change (ΔS) calculated from the DSC curves is approximately as large as 12.63 Jmol⁻¹ K⁻¹, indicating an order-disorder phase transition.²⁴ Such a high $T_{\rm C}$ has never been found in molecular ferroelectrics, which makes the compound applicable under a wide temperature range. Furthermore, we applied second-harmonic generation (SHG) measurement using a polycrystalline sample of 4 to verify the phase transition, because the SHG signal is active in noncentrosymmetric structures, except for three chiral point groups (422, 432, 622). The SHG signal of 4 remains active and stable until the temperature rises above 540 K, confirming a phase transition from a noncentrosymmetric phase to a centrosymmetric phase. Evidently, both the DSC and SHG measurements confirm the phase transition behaviour of 4.

Then, the crystal structures of 1–4 were directly determined by single crystal X-ray diffraction at room temperature (Fig. 2a and Fig. S5 and Table S2, ESI†). At 296 K, [FEtDabco]ZnI₃



Fig. 1 DSC curve and temperature dependent SHG signal of 4.



Fig. 2 (a) The packing view of **4** along the *b*-axis at 296 K; all H atoms were omitted for clarity. (b) The variable-temperature PXRD patterns of **4**. (c) P-E hysteresis loop measured along the *c*-axis at room-temperature using a Sawyer–Tower circuit.

crystallizes in the polar C_{2v} point group with cell parameters a = 19.9308(14) Å, b = 7.8474(5) Å, c = 9.8836(7) Å, and V = 1545.84(18) Å³. The asymmetric unit of **4** is composed of a [FEtDabco]ZnI3 molecule, where the zinc atom is coordinated with three iodine atoms and the unprotonated nitrogen atom in Dabco. The N-C-C-F bond distorts severely and shows a torsion angle of about -68.378° , which possibly induces the symmetry break compared to 3. In addition, comparing the Dabco rings of 3 and 4, the torsion angle of N-C-C-N in Dabco increases from 8.362° to 13.145°, demonstrating the stronger contact existing in [FEtDabco]ZnI3. With regard to the other side of Dabco, the length of Zn-I ranges from 2.53 Å-2.56 Å and the bond length of Zn–N is around 2.12 Å, indicating that all of the atoms are highly ordered and locate in the general positions without any symmetry element. Referring to the specific space group *Pna2*₁, the packing view was observed along the *b*-axis to clarify the origin of the ferroelectricity. It is distinct that all of the fluoroethyl groups are slightly oriented towards the -c direction and the $-ZnI_3$ show an absolutely opposite orientation, inducing the occurrence of a dipole moment and possible ferroelectricity, which is similar to some single-component ferroelectrics.

Due to the excessively high T_c of 4, we conducted variabletemperature powder X-ray diffraction to harvest the high temperature phase structure. As shown in Fig. 2b, most of the diffraction peaks of 4 remain stable under 523 K. When the temperature increased to around 540 K, some diffraction peaks began to transform, manifesting the process of a phase transition. With the temperature heating up to about 563 K, most of the peaks observed in the ferroelectric phase merged and disappeared, which coincides with the DSC and SHG results, and confirms the existence of a phase transition. The paraelectric phase crystal structure was further refined through the Pawley method (Fig. S6, ESI⁺). With the consideration of the large ΔS , which demonstrates a disordered state above $T_{\rm c}$, compound 4 most probably crystallizes in tetragonal point group $P4_2/nmc$ with the cell parameters a = 12.9017 Å, b = 12.9017 Å, c = 21.2949 Å and V = 3544.65 Å³, which is in good agreement with the measured XRD result. The Aizu notation of the ferroelectric-to-paraelectric phase transition is 4/mmmFmm2, indicating that four equivalent polar directions are available in compound 4.25

In order to investigate the intrinsic characteristics of the ferroelectric, we carried out a polarization *versus* electric field measurement using a block single crystal along the polar *c*-axis at room temperature with a frequency of 50 Hz. The well-shaped *P*–*E* hysteresis loop confirms the ferroelectric feature of [FEtDabco]ZnI₃ convincingly (Fig. 2c). The measured remnant polarization (Pr) is approximately equal to 0.24 μ C cm⁻², which is moderate compared to recently reported molecular ferroelectrics based on Dabco and consistent with the calculation result from point charge analysis (Table S3, ESI†). In addition, the relatively low *E*_C (≈5.3 kV cm⁻¹) makes the compound more competitive for practical applications.

For the further design of high performance molecular ferroelectrics, it is highly poignant to gain insight of the smooth symmetry break from Pbca to Pna21 by H/F substitution and the origin of the high $T_{\rm c}$. Therefore, Hirshfeld surface analyses and 2D fingerprint plots were carried out and discussed (the specific descriptions of the Hirshfeld surface can be found in the ESI†).^{26–29} As shown in Fig. 3, the $d_{\rm norm}$ figures of 3 and 4 present a considerable difference triggered by the F atom, in which the significant contacts around the F atom are much more prominent (the deep red circle on the surface) than the intermolecular interactions originated from the H atoms in ethyl. To determine the role of the F atoms, the atom interactions of $F_{\text{inside}} \cdots \text{All}_{\text{outside}}$ and $F_{\text{outside}} \cdots \text{All}_{\text{inside}}$ are highlighted in the 2D fingerprint plots. Obviously, the fluoridation intensifies the contacts between each isolated Dabco molecule and the strong C-F···H-C interactions induce the consistent orientation of all fluoroethyl groups. The iodide atoms also participate in the interactions, which is also pivotal for such a high $T_{\rm C}$. So, it is explicit and logical that the abundant close contacts displayed on the molecule surfaces and the heavy iodide salt 'lock' the rotation of the molecules together and result in the particularly high Curie temperature. The subtle balance between thermodynamics and dynamics realized by H/F substitution should be an inspiration for future design of high $T_{\rm C}$ ferroelectrics.



Fig. 3 The Hirshfeld d_{norm} surfaces and 2D fingerprint plots. (a and b) The d_{norm} surface and fingerprint plot of **3**. (c and d) The d_{norm} surface and fingerprint plot of **4**. (e and f) The close contacts between $F_{inside} \cdots All_{outside}$ and $All_{inside} \cdots F_{outside}$ of **4**.

In order to get valid proof of ferroelectricity, we performed piezo response force microscopy (PFM), which can confirm the ferroelectricity non-destructively and record the structures of domains at the nanoscale.^{30,31} The lateral and vertical piezoelectric signals were recorded at two selected points on the asgrown thin film of **4**. As demonstrated in Fig. 4 and Fig. S7 and S8 (ESI[†]), the typical stripe-like domain structures can be obtained in both phase and amplitude signals. It is worth



Fig. 4 Ferroelectric domains observed in the as-grown thin film of **4** at room-temperature. The phase images along (a) the vertical and (b) the lateral direction. The amplitude images along (c) the vertical and (d) the lateral direction. (e and f) Measured local PFM switching hysteresis loop spectroscopy of **4** at the selected point.

noting that the images collected in the vertical and lateral modes are entirely different. Besides, there scarcely exists any correlation between the phase images and the topography. Hence, these phenomena indicate the emergence of non-180° domains and the characteristics of multiaxial ferroelectricity, which agrees with the Aizu notation of 4/*mmmFmm2* and is an essential property for practical applications in flexible devices. Besides, the conventional hysteresis loops and the butterfly curves are also convincing proof of the switchable ferroelectric domains.

In summary, we successfully modulated the intermolecular interaction and designed an ultra-high $T_{\rm c}$ (540 K) molecular ferroelectric through H/F substitution, [FEtDabco]ZnI₃, which shows sensational features of multiaxial ferroelectricity. This characteristic and the high $T_{\rm c}$ make this compound a potential candidate for practical application as a ferroelectric under extreme conditions. Compared to perovskite and some zerodimensional structures, where the organic components are isolated with the inorganic salt, the metal coordinated with the well modified amine might make more contributions for the enhancement of $T_{\rm c}$. What's more, the design method and the modulation towards intermolecular interaction take full advantage of the flexibility of the building blocks, which is promising for further design of high performance ferroelectrics. We forecast that this work will propel the enrichment of more creationary modification methods, and boost the vigorous development of related fields, like NVMs, sensors and flexible materials.

This work was financially supported by the National Natural Science Foundation of China (21671084).

Conflicts of interest

There are no conflicts to declare.

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