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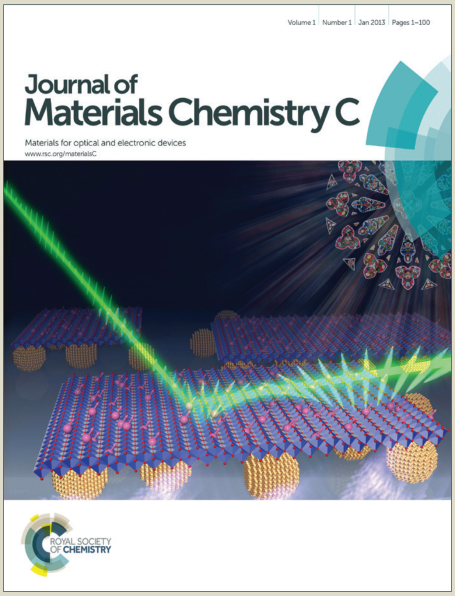

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ARTICLE TYPE

Sequently Switchable Molecular Dielectric Tuned by the Stepwise Ordering in Diisopropylammonium Trifluoromethanesulfonate

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A novel switchable and tunable molecular dielectric material, diisopropylammonium trifluoromethanesulfonate (**1**), which undergoes two reversible second-order solid state phase transitions at 200 K (T_{cL}) and 340 K (T_{cH}) respectively, has been successfully synthesized and grown as bulk crystals. The differential scanning calorimetry (DSC) measurement, dielectric and variable-temperature single-crystal X-ray diffraction studies confirmed the stepwise phase transitions. **1** exhibits a remarkable temperature-dependent dielectric behavior, which could be tuned through three distinctive states triggered by the temperature change. Temperature-dependent single crystal structural analyses of **1** reveal a collection of exceptionally distinct and synchronous molecular motions of both the cationic and anionic moieties in **1**, and the interesting stepwise orderings of cations and anions are mainly responsible for its switchable and tunable dielectric properties. All these demonstrate its potential application as a switchable and tunable molecular dielectric material.

Introduction

Dielectric materials are fundamental components of modern electrical and electronic devices.[1] Among them, switchable molecular dielectrics, which undergo transitions between high and low dielectric states, have attracted great attentions as the promising materials with potential applications in data communication, signal processing, and rewriteable optical data storage, etc.[2] One of the prominent structural design strategies for assembling tunable molecular dielectrics lies in constructing molecular systems to generate distinct molecular motions, such as order-disorder transformations, rotational and orientational motions associated with phase transitions.[3] In most reported cases, only one moiety in a compound could be able to display one-off freezing or ordering, resulting in one single phase transition. This functional moiety could be cation or anion solely, being confirmed in a lot of compounds with the dielectric phase transitions. For instance, Zhang et al. had discovered the amphidynamic crystal exhibiting tunable and switchable dielectric constant originated from an order-disorder phase transition, owing to the dynamical variation of the polar dimethylammonium cation.[4] The order-disorder transformation of diisopropylammonium cation had been found to induce excellent high-temperature ferroelectricity and large dielectric constants.[5-7] In addition to cation, some motion-active anions could also play key role in triggering phase transitions. Dichloroacetate anion with the ordering of unique pendulum-like motions was reported to account for dielectric phase transition in a supramolecular complex.[8] Trifluoromethanesulfonate anion with the obviously distorted bipyramidal geometry accompanied with two distinct motions, namely the "earth rotation" of partial units and the "earth revolution" of the whole molecule, was found to be mainly responsible for the order-disorder phase transition together with the abrupt dielectric anomaly and anisotropy.[9]

Although great work has been devoted to the exploration of new molecular switchable dielectrics, the origin of the pursued switchable dielectric properties is limited in only one functional moiety. It remains unexplored and interesting to search for molecules to realize the synergic effect; namely, combination of both the cation and anion exhibiting freezing motions, especially for the stepwise processes which could lead to sequential dielectric phase transitions. In order to generate such a synergic effect, we propose that two appropriate motion-active moieties should be well-designed and assembled in one compound. Both the cationic and anionic parts are supposed to exhibit distinctive motions, such as ordering or reorientation, which might arouse noteworthy dielectric performances including larger dielectric anomaly in magnitude than that of ordinary phase transitions with only one functional moiety. To testify this assertion, we have explored several potential molecular compounds to see whether such a combination of motion-active cations and anions could result in the synergic effect. Herein, we present a novel switchable molecular dielectric based on two potentially functional blocks of diisopropylammonium cation and trifluoromethanesulfonate anion. As expected, the cation and anion present obviously stepwise ordering process, generating two sequential structural phase transitions and the tunable temperature-dependent dielectric responses among three different states. More surprisingly, in addition to the stepwise ordering, a collection of exceptionally distinct and synchronous molecular motions of both the cationic and anionic parts in diisopropylammonium trifluoromethanesulfonate (**1**) was unprecedentedly discovered.

Experimental section

All chemical reagents were used without further purification. Compound **1** was synthesized through reaction of diisopropylamine (1.01 g, 0.01 mol) and trifluoromethanesulfonic acid (1.50 g, 0.01 mol) in 20 ml water with stirring at room temperature. Colorless block crystals of **1** were obtained by slow evaporation from the aqueous solution after several days (see Supporting Information, Figure S1). The purity of the as-grown crystals was confirmed by the IR spectrum and X-ray powder diffraction matching with the single-crystal structural determination at room temperature (Figure S2, S3).

DSC experiments were performed by heating and cooling the sample (15.17 mg) in the temperature rang 183-363 K on a NETZSCH DSC 200 F3 under nitrogen atmosphere in aluminum crucibles with the heating/cooling rate of 5 K/min. In the dielectric experiments, the single-crystal plates of **1** with silver painted as the electrodes were used for measuring the complex dielectric $\varepsilon = \varepsilon' - i\varepsilon''$. Its dielectric constants were measured using a TH2828 A at the respective frequencies of 100 kHz and 1 MHz with the measuring AC voltage fixed at 1 V.

Table 1. Crystal data and structure refinement of **1** at 355K, 293 K and 170 K.

Moiety formula	$C_7H_{16}F_3NO_3S$	$C_7H_{16}F_3NO_3S$	$C_7H_{16}F_3NO_3S$
Formula weight	251.27	251.27	251.27
Temperature (K)	355(2)	293(2)	170(2)
Crystal system	Tetragonal	Monoclinic	Triclinic
Space group	*P*4/*nmm*	*C*2/*m*	$P\bar{1}$
a/Å	8.9779(6)	12.483(8)	7.9073(8)
b/Å	8.9779(6)	12.806(8)	8.8169(9)
c/Å	8.2260(16)	8.094(5)	8.9215(7)
α/ deg	90	90	90.964(7)
β/ deg	90	94.388(8)	93.394(7)
γ/ deg	90	90	91.206(8)
Volume (Å^3)	663.04(14)	1290.2(14)	620.66(10)
Z	2	4	2
F(000)	232.0	528.0	264.0
Goodness-of-fit on F^2	1.099	1.357	1.050
T_{min}/T_{max}	0.600/1.000	0.859/1.000	0.780/1.000
R_1 (on F_o^2, $I > 2\sigma(I)$)	0.0889	0.0992	0.0635
wR_2 (on F_o^2, $I > 2\sigma(I)$)	0.2618	0.3371	0.2543

$\alpha R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)/\Sigma|F_o|^2]^{1/2}$

Variable-temperature X-ray single-crystal diffraction data at high temperature (**HT**, 355 K) and low temperature (**LT**, 170 K) were collected on Super Nova CCD diffractometer, while the data sets at intermediate temperature (**IT**, 293 K) were collected on Rigaku Saturn Mercury CCD diffractometer. Both of them are equipped with the graphite monochromated Mo-*Kα* radiation (λ = 0.71073 Å). Data collections were using the Crystal Clear software package (Rigaku), while the crystal structures were solved by direct methods and refined by a full-matrix leastsquares method on F^2 data using the SHELXL-97 software package. All non-hydrogen atoms were refined anisotropically and the positions of hydrogen atoms were generated geometrically. Crystalloraphic data and details of data collection and refinement at three temperatures are given in Table 1.

Results and Discussion

For convenience, we label the phase above T_{cH} as the high-temperature phase (**HTP**), the phase between T_{cL} and T_{cH} as intermediate-temperature phase (**ITP**), and the phase below T_{cL} as low-temperature phase (**LTP**). The cell parameters of **1** change remarkably through the three phases (Table 1), and one interesting feature is that the cell volume is doubled in ITP in comparison to those in HTP and LTP. All cell parameters, pronounced b, c axis and volume, change evidently at about 200 K and 340 K respectively for 1 (Fig. S7), revealing the two-step structural phase transitions. The asymmetric unit of **1** contains one diisopropylammonium cation and one deprotonated trifluoromethanesulfonate anion in LTP, then decreases to one-half in ITP and one-quarter in HTP, well consistent with the gradually increasing structural symmetry triggered by the phase transitions during the heating process. From the viewpoint of symmetry breaking, the variable-temperature X-ray single-crystal structure determination reveals that the structure of **1** changes from the tetragonal crystal system with a high centrosymmetric space group of *P*4/*nmm* and the point group D_{4h} at 355 K, firstly to the monoclinic crystal system with an intermediate centrosymmetric space group of *C*2/*m* and the point group C_{2h} at 293 K, and finally to the triclinic crystal system with a low centrosymmetric space group of $P\bar{1}$ and the point group C_i at 170 K. That is, during the cooling process two symmetry breakings occur sequentially with the Aizu notation of 4/*mmmF*2/*m* and 2/$mF\bar{1}$,[10] respectively (Fig. 1). According to the Curie symmetry principle, the space group with broken symmetry of the low-temperature phase is a subgroup of the high-temperature phase (primary phase), *i.e.*, $P\bar{1}$ is a subgroup of *C*2/*m*, which is a subgroup of *P*4/*nmm*.[11]

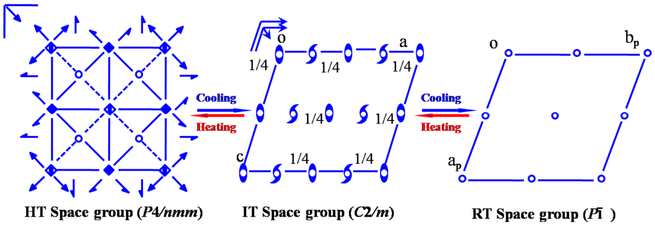

Fig. 1 Spatial symmetry operation change from the **HT** phase (*P*4/*nmm*, no.129) firstly to the **IT** phase (*C*2/*m*, no.12) and finally to the **LT** phase ($P\bar{1}$, no.2) in **1**.

Differential scanning calorimetry (DSC) measurement was carried out to confirm the two reversible structural phase transitions of **1** in the temperature range 173-363 K (Fig. 2). Two pairs of peaks on heating and cooling centered around 200 K and 340 K, along with narrow thermal hysteresis, indicate that **1** undergoes two reversible second-order phase transitions.[12] An entropy change ΔS is estimated with a value of 1.722 J/mol·K around T_{cL}, while around T_{cH} it turns to be 2.569 J/mol·K. Based on the Boltzmann equation, $\Delta S = R\ln N$, where R is the gas constant and N is the ratio of numbers of respective geometrically distinguishable orientations, an estimate of the number of molecular orientations from the calorimetric data yields $N = 1.23$ and 1.36 for the LT and HT phase transitions, respectively. This indicates that **1** is more disordered in HTP than ITP, as well as ITP than LTP; that is, the sequence of disordered degree is HTP>ITP>LTP.[13] Moreover, the comparison of N values between two phase transitions also reveals that **1** undergoes relatively severer structural transformation at T_{cH}.

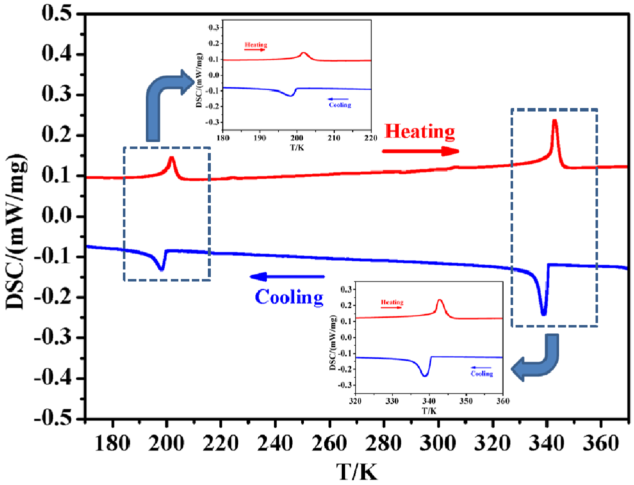

Fig. 2 The DSC curves of **1**.

The disordering of the cation and anion may be statistical or dynamic. In order to check if the disordering is dynamic, temperature-dependence of the real part of the complex dielectric constant was measured in two directions on single-crystal samples of **1**. Both the faces were selected in accordance with the **ITP** structure. Two remarkable anomalies appear at about 200 K and 340 K respectively (Fig. 3), indicating the occurrence of the two sequential phase transitions, well consistent with the temperature dependence of cell parameter changes and DSC results. It can be clearly seen that no obvious dielectric relaxation process is observed in the close vicinity of the transition temperatures under different frequencies (Fig. 3), indicating relatively fast dipolar and molecular motions in this system during the phase transitions.[14] In addition, from the phenomenon of sequential phase transitions in **1**, it seems that the strategy of controlling the stepwise freezing motions of cation and anion is likely to work for obtaining the desired multiple dielectric states. As expected, the result of dielectric measurement verified the conjecture. In the cooling mode, the real part of the dielectric constant along both directions keeps stable until it undergoes an obvious decrease with an abrupt slope at T_{cH} and then remains almost constant, corresponding to the **HT** phase transition. Subsequently, it shows a gradual decrease when the temperature down to T_{cL}, then it decreases sharply with an apparent anomaly at T_{cL}, which correlates with the **LT** phase transition. As discovered above, the dielectric constants could be tuned in three different states, being switched by the two stepwise phase transitions upon temperature changes. A cooling/heating cycle shows a quite narrow thermal hysteresis for both phase transitions (Fig. S6), thus revealing their second-order feature, well consistent with the DSC results. Another striking feature of the dielectric constant of **1** is anisotropic, especially in the vicinity of the phase transitions; namely, the dielectric constants have a crystal-axis dependence. Distinct anomalies are observed during the **HT** phase transition in the direction perpendicular to its four-fold axis (crystallographic *c* axis), while only a small anomaly is recorded along the four-fold axis direction, thus confirming that the dielectric anisotropic properties are confined to the plane perpendicular to the four-fold axis of the **HTP**. From the microscopic viewpoint, the tunable dielectric permittivity closely relates to the positional and orientational variation of molecular dipole moments. It can be seen from the crystal structure that the highly disordered F atoms and O atoms of anion and N atom of cation lie in the plane perpendicular to the c axis (S-C axis) in **HTP** (Fig. 4). The in-plane rotation upon temperature changes yields large dielectric anomaly in the direction within the plane while no dipole-moment component in the c axis, contributing no change of the dielectric permittivity in this direction. However, the slight deviation of S-C axis from c axis in **ITP** leads to the discernable small change. As for the **LT** phase transition process, the structural change is much more complicated, the S-C axis continued to deviate from c axis, which turns out to generate small anomalies for both the two directions. Moreover, when comparing the two phase transitions, the change of dielectric constant of **HT** phase transition is much larger than that of **LT** phase transition, indicating that the former experiences acuter structural variation than the latter, in good agreement with the DSC result.

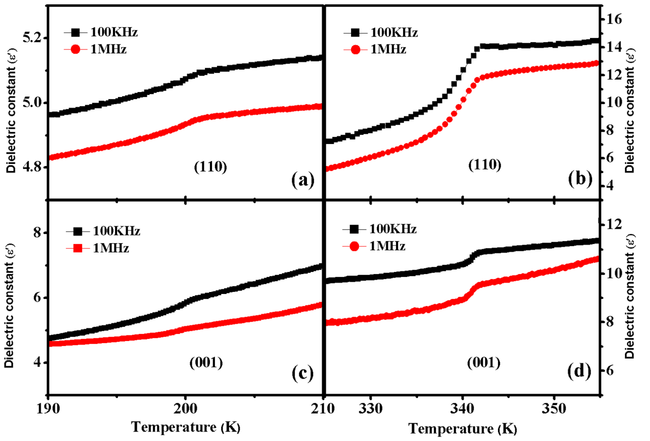

Fig. 3 Temperature dependent of the real part (ε') of the complex dielectric constant measured in the heating mode at 100 KHz and 1 MHz along (110) (a, b) and (001) (c, d) directions, respectively.

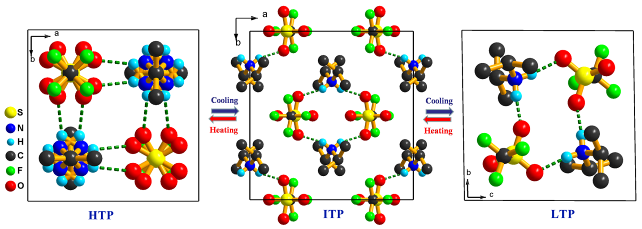

Fig. 4 Structural phase transitions of **1**. The phase transition sequence is **HTP** to **ITP** at about 340 K, and **ITP** to **LTP** at about 200 K.

Although the temperature dependence of cell parameter changes, DSC and dielectric measurements of **1** confirmed the existence of two sequential phase transitions, the intrinsic structural mechanism still remains to be explored. To obtain further insights into the microscopic origin of the phase transitions for **1**, its structural transformations of both cationic and anionic moieties were shown in Fig. 5. It is evident that the C-N-C configuration of the cation persists almost the same in all the three phases, so it's reasonable to appoint it as a reference plane. In the **HTP**, the nitrogen atom N1 of cation is distributed over four equivalent positions. The anion is also disordered with a four-fold symmetry along the S_1-C_1 bond as the rotation axis, while three F atoms are uniformly distributed over four apexes of a square and three O atoms over eight apexes of a octagon, revealing the existence of a highly dynamically disordered anion.[15] It is proposed that both -SO_3 and -CF_3 polyhedrons rotate around the S_1-C_1 bond, which is visually depicted like the earth rotation.[9] Meanwhile, the anionic moiety also behaves in a revolution motion relative to the C-N-C stator plane.

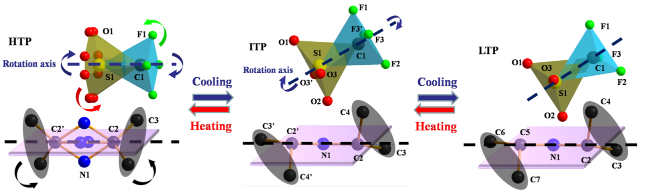

Figure 5. Schematic illustration of the exceptionally distinct and synchronous molecular motions of both the anionic and cationic moieties during the sequential phase transitions.

When the temperature decreases from **HTP** to **ITP**, the -CF_3 polyhedron uplifts away from the plane while the -SO_3 polyhedron falls towards the plane, resulting in the orientational motion of the whole anion, which could be clearly described like the earth revolution. The included angle between S_1-C_1 axis and stator plane changes from 0° in HTP to 59.6° in **ITP**, obviously supporting the earth-revolution-like orientation. Besides, the cationic terminal methyl parts also undergo a corresponding synchronous twisting motion. Namely, the two pairs of terminal methyl groups revolve relative to the stator plane with the similar orientational trace as the earth-revolution-like motion of the anionic moiety. Such twisting motion could be deduced from the distance between the terminal methyl groups to stator plane, which converts from 0.8845 Å (HTP) to 0.1509 (C_3) and 1.2427 Å (C_4) in **ITP**. Meanwhile, the nitrogen atom N1 is frozen into the exclusive position and the cation becomes ordered while the anion still experiences partial disordering. Compared with the highly disordered **HT** state, three F atoms become more ordered and O atoms halve from eight to four, which leads to a lower structural symmetry in **ITP**. This phenomenon reveals the existence of a dynamical disordered anion, disclosing that both -SO_3 and -CF_3 polyhedrons still rotate around the S_1-C_1 axis as depicted like the earth rotation.

With temperature decreasing from **ITP** to **LTP**, the anion becomes totally frozen and thus both moieties exhibit the ordered configuration, giving rise to a slight shift (0.9°) of the included angle between S_1-C_1 axis and stator plane from 59.6° in **ITP** to 58.7° in **LTP**. Meanwhile, the cationic terminal methyl parts also undergo a small twisting motion relative to stator plane, being confirmed by the distance change between the terminal methyl groups and the plane (from 0.1509 and 1.2427 Å to 0.1937/0.1100 and 1.2239/1.2790 Å, respectively). As we are aware, such a collection of exceptionally distinct and synchronous motions of both the cationic and anionic parts in **1** was unprecedentedly discovered during the sequential phase transitions triggered by the temperature change. Impressively, the **HT** phase transition (enhanced one with a synergic effect) with the cooperative orderings of both cation and anion suggests a much severer structural variation than that of **LT** phase transition (ordinary one with only one functional moiety) with only anion experiences ordering process. Such severer structural change reasonably accounts for the observed DSC and dielectric results. Furthermore, all these findings proved it to be feasible to generate such a synergic effect by assembling two well-designed motion-active moieties in order to obtain superior dielectric properties such as large dielectric anomaly.

Conclusion

In summary, we have presented a novel switchable molecular dielectric, which undergoes two sequential reversible phase transitions at 200 K and 340 K respectively. A collection of exceptionally distinct and synchronous molecular motions of both the cationic and anionic moieties in this well-designed compound has been unprecedentedly discovered. The associated dielectric constants could be tuned through three distinctive states, which are externally switched by the two phase transitions upon temperature changes, and could be intrinsically ascribed to the stepwise ordering process of both the cation and anion. It is expected that our findings will provide new impetus for the development of promising strategies to construct dielectric materials.

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Notes

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†Electronic Supplementary Information (ESI) available: CIF file, PXRD pattern, the dielectric constant measured in the cooling and heating cycle.

References

1 (a) P. Simon, Y. Gogotsi, *Nat. Mater*. 2008, **7**, 845-854; (b) P. A. Kohl, *Annu. Rev. Chem. Biomol. Eng*. 2011, **2**, 379-401.

2 (a) M. Wuttig, N. Yamada, *Nat. Mater*. 2007, **6**, 824-832; (b) M. Salinga, M. Wuttig, *Science* 2011, **332**, 543-544; (c) D. Lencer, M. alinga, M. Wuttig, *Adv. Mater*. 2011, **23**, 2030-2058; (d) L. B. Kong, S. Li, T. S. Zhang, J. W. Zhai, F. Y. C. Boey, J. Mad, *Prog. Mater. Sci*. 2010, **55**, 840-893; (e) H. Zheng, J. B. Rivest, T. A. Miller, B. Sadtler, A. Lindenberg, M. F. Toney, L. W. Wang, C. Kisielowski, A. P. Alivisatos, *Science* 2011, **333**, 206-209.

3 (a) T. Akutagawa, S. Takeda, T. Hasegawa, T. Nakamura, *J. Am. Chem. Soc*. 2004, **126**, 291-294; (b) R. Jakubast, Z. Galewskit, L. Sobczyk, J. Matuszewskit, *J. Phys. C: Solid State Phys*. 1985, **18**, L857-L860; (c) S. Horiuchi, Y. Tokura, *Nat. Mater*. 2008, **7**, 357-366.

4 W Zhang, H. Y. Ye, R. Graf, H. W. Spiess, Y. F. Yao, R. Q. Zhu, R. G. Xiong, *J. Am. Chem. Soc*. 2013, **135**, 5230-5233.

5 D. W. Fu, W. Zhang, H. L. Cai, J. Z. Ge, Y. Zhang, R. G. Xiong, *Adv. Mater*. 2011, **47**, 5658-5662.

6 D. W. Fu, H. L. Cai, Y. Liu, Q. Ye, W. Zhang, Y. Zhang, X. Y. Chen, G. Giovannetti, M. Capone, J. Li, R. G. Xiong, *Science* 2013, **339**, 425-428.

7 D. A. Bonnell, *Science* 2013, **339**, 401-402.

8 S. G. Li, J. H. Luo, Z. H. Sun, S. Q. Zhang, L. N. Li, X. J. Shi, M. C. Hong, *Cryst. Growth Des*. 2013, **13**, 2675-2679.

9 Z. H. Sun, J. H. Luo, T. L. Chen, L. N. Li, R. G. Xiong, M. L. Tong, M. C. Hong, *Adv. Funct. Mater*. 2012, **22**, 4855-4861.

10 K. Aizu, *Phys. Rev. B* 1970, **2**, 754-772.

11 Z. H. Sun, X. Q. Wang, J. H. Luo, S. Q. Zhang, D. Q. Yuan, M. C. Hong, *J. Mater. Chem. C*, 2013, **1**, 2561-2567.

12 (a) Z. Pająk, P. Czarnecki, B. Szafrańska, H. Małuszyńska, Z. Fojud, *J. Chem. Phys*. 2006, **124**, 144502; (b) H. Y. Ye, J. Z. Ge, F. Chen, R. G. Xiong, *CrystEngComm,* 2010, **12**, 1705-1708; (c) D. W. Fu, W. Zhang, H. L. Cai, Y. Zhang, J. Z. Ge, R. G. Xiong, S. D. Huang, T. Nakamura, *Angew. Chem. Int. Ed.* 2011, **50**, 11947-11951; (d) X. J. Shi, J. H. Luo, Z. H. Sun, S. G. Li, C. M. Ji, L. N. Li, L. Han, S. Q. Zhang, D. Q. Yuan, M. C. Hong, *Cryst. Growth Des*. 2013, **13**, 2081-2086.

13 P. Jain, V. Ramachan, R. J. Clark, H. D. Zhou, R. H. Toby, N. S. Dalal, H. Kroto, A. K. Cheetham, *J. Am. Chem. Soc*. 2009, **131**, 13625-13627.

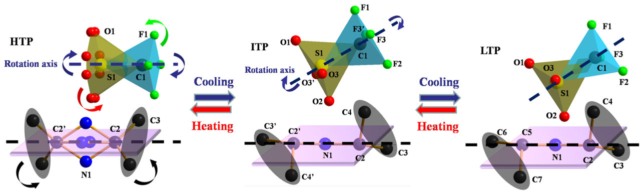
14 (a) R. Jakubas, A. Piecha, A. Pietraszko, G. Bator, *Phys. Rev. B* 2005, **72**, 104-107; (b) B. Kulicka, V. Kinzhybalo, R. Jakubas, Z. Ciunik, J. Baran, W. Medycki, *J. Phys. Condens. Matter* 2006, **18**, 5087-5104.

15 W. Zhang, Y. Cai, R. G. Xiong, H. Yoshikawa, K. Awaga, *Angew. Chem*. 2010, **122**, 6758-6760.

Table of contents (TOC)

Sequently Switchable Molecular Dielectric Tuned by the Stepwise Ordering in Diisopropylammonium Trifluoromethanesulfonate

Pan Zhou, Zhihua Sun, Shuquan Zhang, Chengmin Ji, Sangen Zhao, Rengen Xiong, Junhua Luo*



Diisopropylammonium Trifluoromethanesulfonate, a switchable molecular dielectric, undergoes two sequential phase transitions and exhibits sequently switchable dielectric behaviour aroud 200 and 340 K respectively.