Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Dual-channel control of ferroelastic domains in a host-guest inclusion compound

Jun-Chao Liu,‡ Fang-Fang Di,‡ Yi-Piao Zeng,‡ Wu-Jia Chen,† Xiao-Yun Huang, Yan-Ling Luo, Xuan Zhu, Lin Zhou* and Yuan-Yuan Tang*

Ordered Matter Science Research Center, Nanchang University, Nanchang 330031, People's Republic of China. E-mail: zhoulin@ncu.edu.cn; tangyuanyuan@ncu.edu.cn.

Experimental section

Experimental section

Synthesis Method. All of the chemical reagents in the synthesis were of reagent grade and used without further purification. 3,4-Difluoroaniline, 18-crown-6, and bis(trifluoromethanesulfonyl)-amine were dissolved in an appropriate amount of methanol in equal stoichiometric ratios. Finally, the colorless and transparent single crystals of [(3,4-DFA)(18-crown-6)][TFSA] were obtained by slow evaporation of methanol at room temperature.

Single-crystal X-ray crystallography. Single-crystal X-ray diffraction data at different temperatures were measured using a Rigaku Saturn 924 diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Data collection and structural refine were performed using Rigaku CrystalClear and SHELXTL software package. The crystal data and structure refinement are summarized in Table S1. The X-ray crystallographic structures have been deposited at the Cambridge Crystallographic Data Centre (deposition numbers CCDC: 2202555 and 2202556) and can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/getstructures.

Powder X-ray diffraction (PXRD). PXRD data were measured on a Rigaku D/MAX 2000 PC X-ray diffractometer with Cu Kα radiation at room temperature. Diffraction patterns were collected in the 2θ range of 5–50° with a step size of 0.02°.

Thermal analyses measurements. Differential scanning calorimetry (DSC) measurements were performed using a NETZSCH DSC 200F3 instrument. The powder samples were placed in aluminum crucibles and measured under a nitrogen atmosphere at heating and cooling rates of 20 K min^{-1}. Thermogravimetric analyses (TGA) were carried out on a PerkinElmer TGA 8000 instrument by heating crystalline samples with a rate of 30 K min^{-1} under a nitrogen atmosphere.

Dielectric measurements. The dielectric measurements were carried on a TH2828A impedance analyzer for [(3,4-DFA)(18-crown-6)][TFSA] from 500 Hz to 1 MHz. The pressed-powder pellets were deposited with silver conducting glue used as electrodes.

Infrared (IR) spectra. The infrared spectrum was analyzed with Bruker INVENIO, as shown in Fig. S1. The broad peak at 3656-3287 cm^{-1} corresponds to the N–H stretching vibration. The strong peak at 3019-2885 cm^{-1} is the aromatic ring C–H stretching vibration. The strong peak at 1354 cm^{-1} is the absorption peak of crown ether. The strongest peak at 1231-1154 cm^{-1} corresponds to the C–O stretching vibration, and several strong peaks at 1131-1052 cm^{-1} are absorption peaks of [TFSA].

Ferroelastic measurements. The precursor solution of [(3,4-DFA)(18-crown-6)][TFSA] was prepared by dissolving 20 mg of the crystals in 400 μL. Then, a 20 μL precursor solution was spread on a clean indium-doped tin oxide (ITO) glass substrate. The thin films were prepared by heat treatment at 313 K for 30 min and then annealed at 343 K for 5 min. Surface morphology and ferroelastic domain observations of thin films were performed on Olympus BX53-P polarized light microscope. The stress is applied by manual pressure with the tip of a needle.

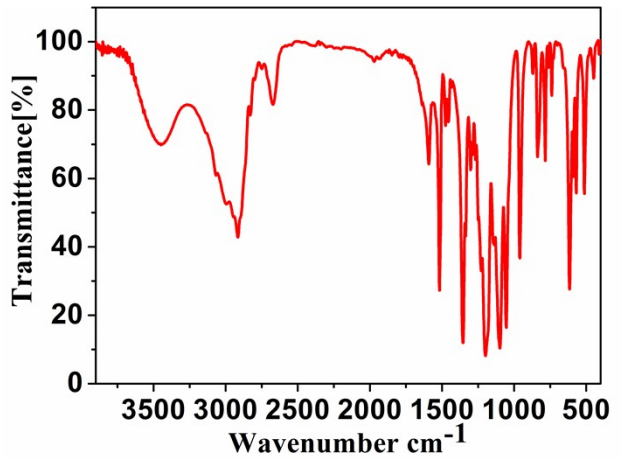

Fig. S1 The IR spectrum of [(3,4-DFA)(18-crown-6)][TFSA] was recorded with Bruker INVENIO.

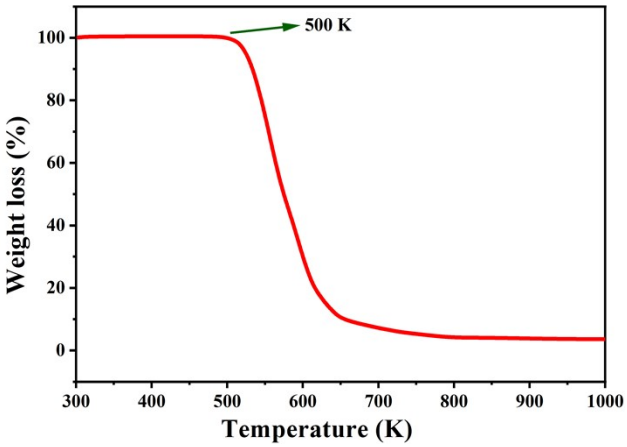

Fig. S2 TGA curve of [(3,4-DFA)(18-crown-6)][TFSA]. TGA test results show that [(3,4-DFA)(18-crown-6)] [TFSA] is stable until 500 K.

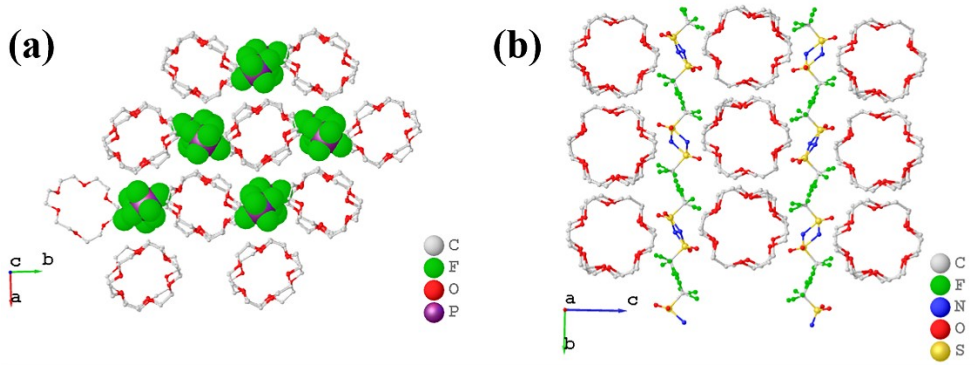

Fig. S3 (a) Packing view of crystal structures of [(3,4-DFA)(18-crown-6)][PF_6] at 298 K. (b) Packing view of crystal structures of [(3,4-DFA)(18-crown-6)][TFSA] at 273 K.

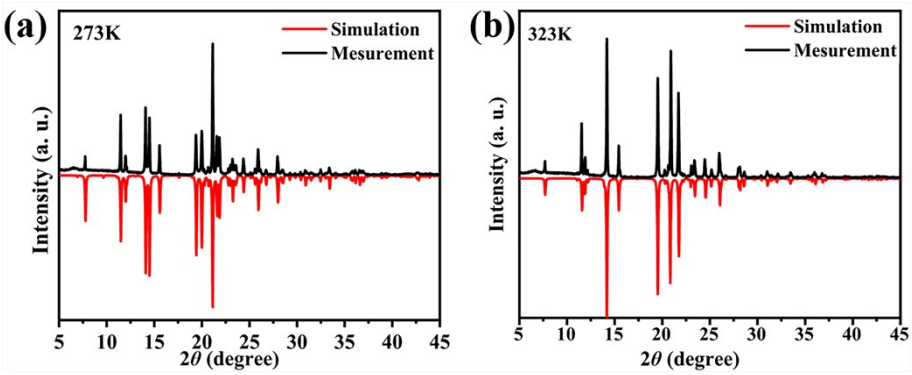

Fig. S4 The experimental and simulated PXRD patterns at 273 K (a) and 323 K (b), respectively.

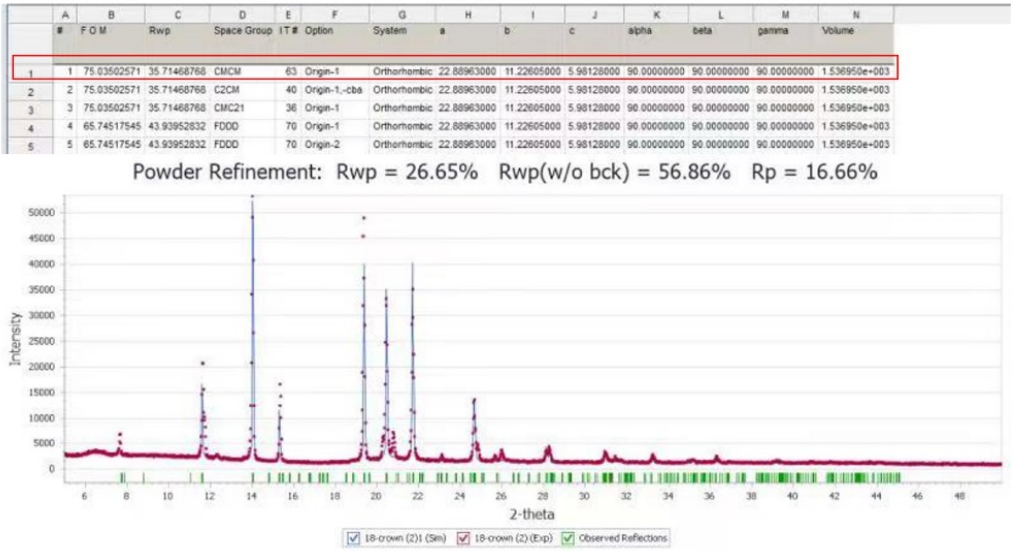

Fig. S5 Structural refinement results of PXRD data for [(3,4-DFA)(18-crown-6)][TFSA] in HTP. The indexing of PXRD data reveals an orthorhombic lattice, and through the Pawley refinements, we obtained

the orthorhombic point group *mmm*, among which the most possible space group is *Cmcm*. The refined cell parameters are a = 22.8896 Å, b = 11.2260 Å, c = 5.9812 Å.

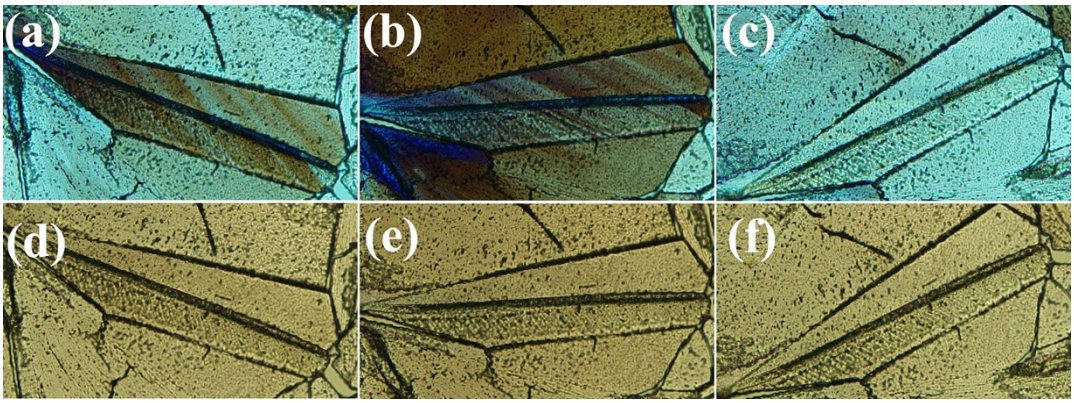

Fig. S6 The ferroelastic domains of [(3,4-DFA)(18-crown-6)][TFSA] at 298 K.

Table S1. Crystal data and structure refinement for [(3,4-DFA)(18-crown-6)][TFSA].

Compound	[(3,4-DFA)(18-crown-6)][TFSA]	
Formula	$C_{20}H_{30}F_8N_2O_{10}S_2$	
Temperature	273 K	323 K
Formula weight	674.58	674.58
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	*Pnma*
a (Å)	8.3948(3)	15.2739(8)
b (Å)	15.3922(6)	22.9415(11)
c (Å)	22.7435(7)	8.5182(6)
β (deg)	92.020(4)	90
V (Å^3)	2936.96(18)	2984.8(3)
Z, D_{calc} / g cm^{-3}	4, 1.526	4, 1.501
Goodness-of-fit on F^2	1.082	1.088
R_{int}	0.0415	0.0183
R_1 (> 2σ)	0.1487	0.1332
wR_2 (> 2σ)	0.2536	0.1687

Table S2. Hydrogen bonds for [(3,4-DFA)(18-crown-6)][TFSA] in RTP and ITP, respectively.

	D-H···A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
273 K	N1—H1A···O2A	0.89	2.88	3.38(6)	116.8
	N1—H1A···O1A	0.89	2.01	2.86(5)	158.7
	N1—H1A···O1	0.89	1.97	2.847(9)	170.8
	N1—H1B···O5A	0.89	1.96	2.85(4)	171.2
	N1—H1B···O5	0.89	2.01	2.869(8)	162.0
	N1—H1C···O3A	0.89	1.86	2.75(4)	171.5
323 K	N1—H1A···O5	0.89	2.12	2.794(7)	131.8
	N1—H1B···O2	0.89	2.06	2.865(10)	149.0