Supporting information

Unusual High-Temperature Reversible Phase-Transition Containing Dielectric and Nonlinear Optical Switch in a Host-Guest Supramolecular Crown Ether Clathrate

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Experimental section

Preparation of Thin Films All analytical grade chemicals were purchased from Energy Chemical and used without further purification. Firstly, the sample was dissolved into DMF to form a homogeneous precursor solution. Then, abovementioned precursor solution was carefully dropped on a freshly cleaned substrate [poly(ethylene terephthalate) (PET)]. With controlled substrate temperature and a rotary speed of 6000 rpm, compact and uniform thin films with high coverage were in situ grown on the flexible substrate.

Single-crystal X-ray crystallography Single-crystal X-ray diffraction data of 1 were

collected at 293 K and 203 K on a Rigaku Saturn 724 diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å). Data processing and empirical absorption correction were performed using the Crystalclear software package (Rigaku, 2005). The crystal structures were solved by direct methods, and refined by full-matrix least-squares refinements based on F^2 by using the SHELXLTL software package (SHELX-2014). All non-H atoms were refined anisotropically using reflections with $I > 2\sigma(I)$. All hydrogen atoms were generated geometrically and refined using the 'riding' model with Uiso = 1.2 Ueq (C and N). The asymmetric units and the packing views were drawn by using DIAMOND (Brandenburg and Putz, 2005). Some bond distances and angles were calculated by using DIAMOND, and other calculations were calculated out by using SHELXLTL. A summary of the crystallographic data and structure refinement details of **1** at 293 K and 203 K were given in Table S1.

Physical measurements Differential scanning calorimetry (DSC) measurement was implemented using a Perkin-Elmer Diamond DSC instrument by heating and cooling the crystalline samples (9.8 mg) over the temperature range of 200 K–380 K under nitrogen at atmospheric pressure in aluminum crucibles with a rate of 10 K/min. Powder X-ray diffraction (PXRD) was measured on a Rigaku D/MAX 2000 PC X-ray diffractometer instrument in the 2θ range of 5°–52° with a step size of 0.02°. Dielectric measurement was performed on a Tonghui TH2828A instrument between 160 K–380 K over the frequency range from 8 kHz to 1000 kHz with an applied electric field of 1 V. Variable-temperature second harmonic generation (SHG) experiment was collected on an Ins 1210058, INSTEC Instrument with the laser Vibrant 355 II, OPOTEK (pulsed Nd:YAG at a wavelength of 1064 nm, 1.6 MW peak power, 5 ns pulse duration, 10 Hz repetition rate). The numerical values of the nonlinear optical coefficients for SHG have been determined by comparison with a KDP reference.



Fig. S1 Colorless block crystal of compound 1.



Fig. S2 Transparent thin film was fabricated on PET substrate plane by spin-coating method.



Fig. S3 Infrared (IR) spectra of solid **1** in KBr pellet recorded on a Shimadzu model IR-60 spectrometer at room temperature.



Fig. S4 Experimental powder diffraction (PXRD) pattern of compound 1 matches very well with the simulated pattern in terms of the crystal structures at room temperature.



Fig. S5 Crystal-packing views along the *c*-axis of compound 1 at 203 K (a) and 293 K (b), the hydrogen atoms except for N-H being omitted for clarity.



Fig. S6 Variable-temperature PXRD patterns of compound 1.



Fig. S7 Rietveld refinement by the MS program of compound 1 at 358 K. As a result of the plot fitting, the high temperature structure should belong to a monoclinic system with a = 14.781 Å, b = 10.653 Å, c = 9.097 Å, $a = \gamma = 90.00(0)^\circ$, $\beta = 104.57(0)^\circ$. In addition, we found that the MS-fited monoclinic unit cell parameters are close to crystallographic data were collected using a Rigaku CCD diffractometer with Mo-Ka radiation with a = 8.747 Å, b = 15.486 Å, c = 9.46 Å, $a = \gamma = 90.00(0)^\circ$, $\beta = 104.54(1)^\circ$. Based on the symmetry principle and the corresponding physical properties, we guessed that the high temperature structure should belong to *P*c or *P*2₁ space group of the monoclinic system.



Fig. S8 (a) Temperature-dependence of the real part (ε') of the polycrystalline samples of **1** at 1 MHz upon heating and cooling. (b) The imaginary part (ε'') of the dielectric permittivity measured at different frequencies on cooling course for the polycrystalline sample; the insert is Arrhenius plots for the dielectric relaxation on cooling, the calculated values of activation energy *Ea* and relaxation time τ_0 were estimated to be 0.766 eV and 2.684 × 10⁻¹⁸ s, respectively.



Fig. S9 Temperature-dependence of the real part (ε') of the polycrystalline samples of 1 at 100 kHz upon heating and cooling within the range of 300 K–380 K (a) and 150 K–380 K (b).

Table S1.	Crystal	data and	structure	refinements	for co	mpound 1	at LTP	and ITP.
	2					1		

Molecular formula	$C_{18}H_{30}F_2NO_{10}Cl$	$C_{18}H_{30}F_2NO_{10}Cl$
T/K	203 K	293 K
Formula weight	493.88	493.88
Crystal system	orthorhombic	orthorhombic
Space group	$Pca2_1$	$Pca2_1$
<i>a</i> / Å	14.558(5)	14.5486(9)
b / Å	11.247(4)	11.2914(7)
<i>c</i> / Å	14.392(5)	14.5674(8)
$V/ Å^3$	2356.3(13)	2393.0(2)
Ζ	4	4
$D_{ m calc}$ / g·cm ⁻³	1.389	1.368

μ / mm^{-1}	0.229	0.226
F(000)	1040	1036
T_{\min} / T_{\max}	0.929 / 0.938	0.816 / 1.00
Reflns collected	16630	11819
Independent reflns	5200	5598
$R_{ m int}$	0.0710	0.019
No. of parameters	319	328
$R_1^{[a]}, wR_2^{[b]} [I > 2\sigma(I)]$	0.1402 / 0.3273	0.0413 / 0.1015
R_1 , wR_2 [all data]	0.1599 / 0.3392	0.0738 / 0.1156
GOF	1.081	1.015
$\Delta ho^{[c]} / e \cdot Å^{-3}$	0.818 / -0.570	0.170 / -0.158

[a] $R_1 = \Sigma ||F_0| - |F_c|| / |F_0|$. [b] $wR_2 = [\Sigma w (F_0^2 - F_c^2)^2] / \Sigma w (F_0^2)^2]^{1/2}$. [c] Maximum and minimum residual electron density.

Table S2. Selected bond lengths [Å] and angles [°] for compound $[(C_6H_5NF_2)(18-crown-6)][HClO_4]$ at 203 K and 293 K.

203 K			
F1—C15	1.39 (2)	C11—C15—C17	122.3 (16)
F2—C17	1.34 (2)	C11—C15—F1	122.3 (17)
N1—C13	1.468 (15)	C17—C15—F1	115.4 (19)
C15—C17	1.35 (3)	C15—C17—F2	117.4 (16)
C15—C11	1.32 (3)	C19—C17—F2	118.4 (16)
C17—C19	1.40 (2)	C15—C17—C19	123.6 (18)
C11—C18	1.35 (2)	C15—C11—C18	116.4 (17)
C13—C19	1.36 (2)	C19—C13—C18	120.9 (13)
C13—C18	1.407 (19)	C19—C13—N1	121.5 (12)
Cl1—O10	1.397 (16)	C18—C13—N1	117.6 (12)
Cl1—O8A	1.417 (17)	C11—C18—C13	122.9 (18)
Cl1—O9A	1.424 (14)	C13—C19—C17	113.7 (15)
Cl1—07	1.425 (10)	08A-Cl1-09A	114.4 (13)
Cl1—O10A	1.434 (17)	010-Cl1-07	116.8 (11)
Cl1—O9	1.459 (17)	08A—Cl1—O7	111.4 (12)
Cl1—08	1.472 (17)	09A—Cl1—07	106.1 (11)
		08A-Cl1-010A	106.4 (13)
		O9A-Cl1-O10A	110.3 (13)
		O7-Cl1-O10A	108.2 (12)
		010-Cl1-09	111.2 (14)
		O7—Cl1—O9	107.1 (11)
		010-Cl1-08	101.3 (13)
		O7—Cl1—O8	110.2 (11)
		O9—Cl1—O8	110.0 (13)
202 V			

F1—C15	1.360 (5)	C13—C18—C11	119.9 (4)
F2—C17	1.270 (5)	C11—C15—C17	120.8 (4)
F2A—C11	1.260 (9)	C11—C15—F1	120.3 (4)
N1-C13	1.457 (4)	C17—C15—F1	119.0 (5)
C15—C11	1.359 (7)	F2—C17—C15	115.9 (4)
C15—C17	1.342 (6)	F2—C17—C19	122.9 (5)
C17—C19	1.381 (5)	C15—C17—C19	120.8 (4)
C11—C18	1.374 (6)	F2A—C11—C15	104.6 (6)
C13—C18	1.374 (4)	F2A—C11—C18	129.6 (7)
C13—C19	1.355 (4)	C15—C11—C18	119.2 (4)
Cl1010A	1.340 (8)	C18—C13—C19	120.4 (3)
Cl1—O8A	1.353 (7)	C18—C13—N1	119.9 (4)
Cl1—O10	1.380 (5)	C19—C13—N1	120.6 (3)
Cl1—09	1.362 (6)	C13—C19—C17	118.8 (4)
Cl1—O9A	1.380 (10)	O10A—Cl1—O8A	109.1 (9)
Cl1—07	1.399 (3)	O9—Cl1—O10	108.8 (6)
Cl1—O8	1.413 (6)	010A-Cl1-09A	106.3 (9)
		08A-Cl1-09A	106.0 (8)
		O10A—Cl1—O7	109.0 (6)
		08A—Cl1—O7	110.7 (5)
		09—Cl1—O7	108.0 (4)
		010-Cl1-07	110.1 (3)
		09A—Cl1—O7	115.6 (5)
		09—Cl1—O8	109.5 (6)
		O10-Cl1-O8	106.6 (6)
		07—Cl1—O8	113.8 (3)

Table S3. Hydrogen-bond parameters (Å, °) for compound $[(C_6H_5NF_2)(18\text{-crown-6})]$ [HClO₄] at 203 K and 293 K.

	D—H…A	H···A	D····A	D—H…A
203 K	N1—H1E…O6 ⁱ	2.03	2.923 (9)	170
	N1— $H1C$ ···O4 ⁱ	2.01	2.880 (11)	163
	$N1 - H1D \cdots O2^i$	1.97	2.856 (10)	166
293 K	N1—H1D…O1 ⁱⁱ	2.39	2.939 (3)	121
	N1—H1E····O2 ⁱⁱ	1.99	2.838 (3)	160
	N1—H1E···O3 ⁱⁱ	2.38	2.930 (3)	120
	N1—H1C····O4 ⁱⁱ	2.06	2.907 (3)	160
	N1—H1C···O5 ⁱⁱ	2.37	2.916 (4)	120
	N1—H1D····O6 ⁱⁱ	2.02	2.865 (3)	160

Symmetry codes: (i) -*x*+1, -*y*+1, *z*-1/2; (ii) -*x*+1, -*y*+1, *z*+1/2.