Supporting information

Water motion-controlled reversible phase transition and de/absorption-controlled reversible phase transformation in hydrate crystal (BEDABCO)ClO4·H2O and its analogs

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Contents:

Experimental section

Materials and methods

All the analytical grade chemicals were used as received without further purification. Elemental analysis was performed on a vario MICRO analyzer. Infrared (IR) spectra were recorded on a Nicolet 5700 spectrometer. Thermogravimetric analysis (TGA) was carried out on a METTLER TOLEDO STARe System. Measurements of differential scanning calorimetry (DSC) were performed on a Perkin-Elmer Diamond DSC instrument from 130 to 293 K and the heating rate is 10 K/min at atmospheric pressure. Powder X-ray diffraction (PXRD) was measured on a Rigaku SmartLab X-ray diffraction instrument. Dielectric measurements were performed on a TongHui 2828 impedance Analyzer over the frequency range from 500 Hz to 1 MHz and the temperature range from 280to 360 K with an applied electric field of 1.0 V.

Synthesis of compounds 1 – 4

Compound **1-2**

1,4-Diazabicyclo [2.2.2]octane (1.12 g, 10 mmol) and 1,2-dibromoethane (1.88 g, 10 mmol) were mixed in 20 ml of chloroform and refluxed at 343 K for 4 hours. then filter the solid in the solution and dissolve these solid into 20 ml water and add $NaClO_4 \cdot H_2O$ (1.4046 g, 10 mmol) with stirring, after several days, colorless crystals **1** were obtained by slow evaporation the solvent with a yield of 74%.

Crystals of **2** were obtained via re-crystallizing compound **1** five times in D_2O.

Compound **3**

1,4-Diazabicyclo [2.2.2]octane (1.12 g, 10 mmol) and 1-Bromo-2-chloroethane (1.43 g, 10 mmol) were mixed in 20 ml of chloroform and refluxed at 343 K for 4 hours. then filter the solid in the solution and dissolve these solid into 20 ml water and add $NaClO_4 \cdot H_2O$ (1.4046 g, 10 mmol) with stirring, after several days, colorless crystals **3** were obtained by slow evaporation the solvent with a yield of 84%.

Compound **4**

1,4-Diazabicyclo [2.2.2]octane (1.12 g, 10 mmol) and 1-Bromo-2-chloroethane (1.43 g, 10 mmol) were mixed in 20 ml of chloroform and refluxed at 343 K for 4 hours.

then filter the solid in the solution and dissolve these solid into 20 ml water and add $NaBF_4 \cdot H_2O$ (1.10 g, 10 mmol) with stirring, after several days, colorless crystals **4** were obtained by slow evaporation the solvent with a yield of 68%.

Crystal structure measurement

Single-crystal data of **1** were collected at different temperatures on a Rigaku Saturn 724^+ diffractometer equipped with a Rigaku low-temperature gas spray cooler device by using Mo-Kα (λ = 0.71075 Å) radiation from a graphite monochromator. Data processing was performed using the CrystalClear software package (Rigaku, 2005). The structures were solved by direct methods and successive Fourier synthesis and then refined by full-matrix least-squares refinements on F^2 using the SHELXL-2014 software package. Hydrogen atoms bonded to the carbon atoms were placed in calculated positions and refined as a riding mode, with C−H = 0.96 Å (methylene) with $U_{iso}(H) = 1.2\ U_{eq}(C)$. Summary of crystallographic data for the compounds are given in Table 1. CCDC 1473188-1473193 contain the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Table S1 Crystal data of **1**

		1	
T / K	293(2)	333(2)	343(2)
Formula	$C_8H_{18}BrClN_2O_5$	$C_8H_{18}BrClN_2O_5$	$C_8H_{18}BrClN_2O_5$
Formula weight	337.59	337.59	337.59
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / Å	10.980(2)	11.055(6)	11.067(2)
b / Å	10.333(2)	10.452(6)	10.483(2)
c / Å	11.370(2)	11.388(6)	11.404(2)
α / °	90	90	90
β /°	93.92(3)	94.249(9)	94.32(3)
γ /°	90	90	90

V / Å^3	1287.0(5)	1312.3(12)	1319.3(5)
Z	4	4	4
D_{calc} / g·cm^{-3}	1.742	1.709	1.700
μ / mm^{-1}	3.413	3.348	3.330
F(000)	688	688	688
θ range / °	3.180−27.469	2.685−27.556	3.146−27.474
Reflns collected	8773	14041	4766
Independent reflns (R_{int})	2954 (0.0424)	3029 (0.0597)	3022 (0.0669)
no. parameters	160	160	160
R_1[a], wR_2[b] [I>2σ(I)]	0.0427, 0.0921	0.0521, 0.0974	0.0576, 0.1074
R_1, wR_2 [all data]	0.0558, 0.098	0.0800, 0.1070	0.1310, 0.1336
GOF	1.088	1.110	0.972
$\Delta\rho$[c] / e·Å^{-3}	0.403, −0.704	0.475, −0.524	0.347, −0.422

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

Table S1 Crystal data of **2-4**

	2	**3**	**4**
T / K	293(2)	293(2)	293(2)
Formula	$C_8H_{16}BrClD_2N_2O_5$	$C_8H_{18}Cl_2N_2O_5$	$C_8H_{18}BBrF_4N_2O$
Formula weight	339.60	293.14	324.95
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / Å	11.018(2)	10.919(2)	10.886(2)
b / Å	10.388(2)	10.331(2)	10.237(2)
c / Å	11.406(2)	11.330(2)	11.376(2)
α / °	90	90	90
β /°	94.03(3)	94.06(3)	94.16(3)
γ /°	90	90	90
V / Å^3	1302.2(5)	1274.9(4)	1264.4(4)
Z	4	4	4
D_{calc} / g·cm^{-3}	1.732	1.527	1.707
μ / mm^{-1}	3.373	0.521	3.286
F(000)	688	616	585
θ range / °	3.165−27.482	3.187−27.482	3.196−27.484
Reflns collected	13080	8606	8495
Independent reflns (R_{int})	2988 (0.0766)	2932 (0.0300)	2898 (0.0802)
no. parameters	160	161	160
R_1[a], wR_2[b] [I>2σ(I)]	0.0460, 0.1014	0.0436, 0.1037	0.0649, 0.1464
R_1, wR_2 [all data]	0.0634, 0.1094	0.0569, 0.1105	0.0984, 0.1692
GOF	1.045	1.055	0.967
$\Delta\rho$[c] / e·Å^{-3}	0.489, −0.554	0.467, −0.321	0.709, −1.010

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

minimum residual electron density.

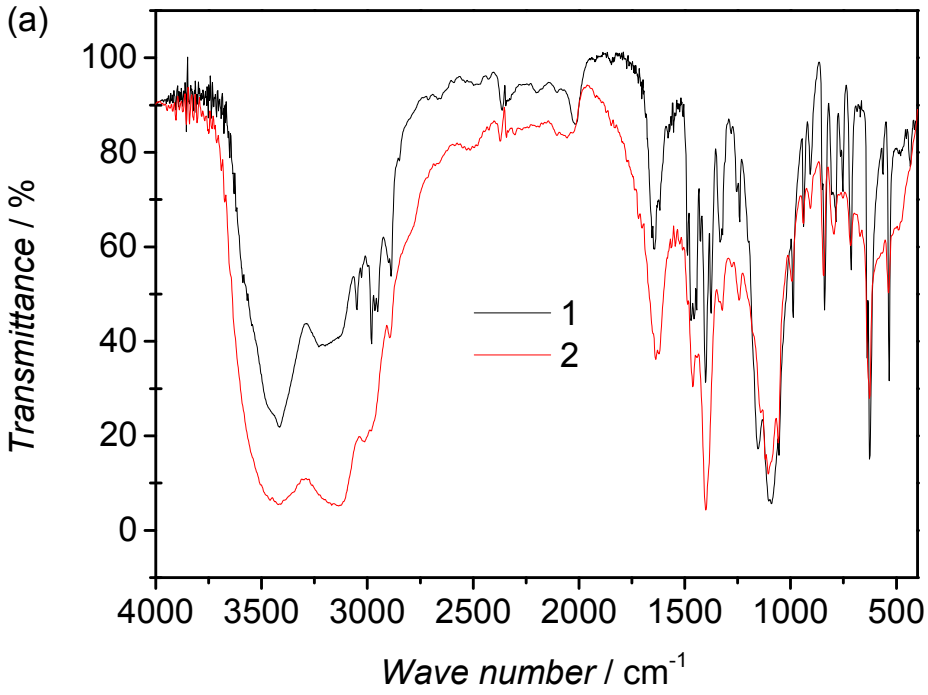
Table S2 Hydrogen bond of crystal **3** and **4** at 293 K (Å, °).

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
3				
O(5)-H(5WA)...N(2)	0.833(17)	2.13(2)	2.930(3)	160(3)
O(5)-H(5WB)...O(2)#1	0.846(17)	2.21(2)	3.017(3)	161(3)
4				
O(1)-H(1WA)...N(2)	0.840(19)	2.14(4)	2.920(6)	154(7)
O(1)-H(1WB)...F(2)#1	0.86(2)	2.12(3)	2.950(6)	164(6)

Symmetry code: #1 x, -y+3/2, z-1/2.

Table S3 Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($A^2 \cdot 10^3$) for O5 in crystal 1 at 343 K, 333 K and 293 K. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

ATOM	X	Y	Z	U_{eq}
343 K				
O(5)	4821(5)	8147(7)	457(5)	99(2)
333 K				
O(5)	4812(3)	8166(4)	473(4)	89(1)
293 K				
O(5)	4817(3)	8189(3)	476(3)	74(1)



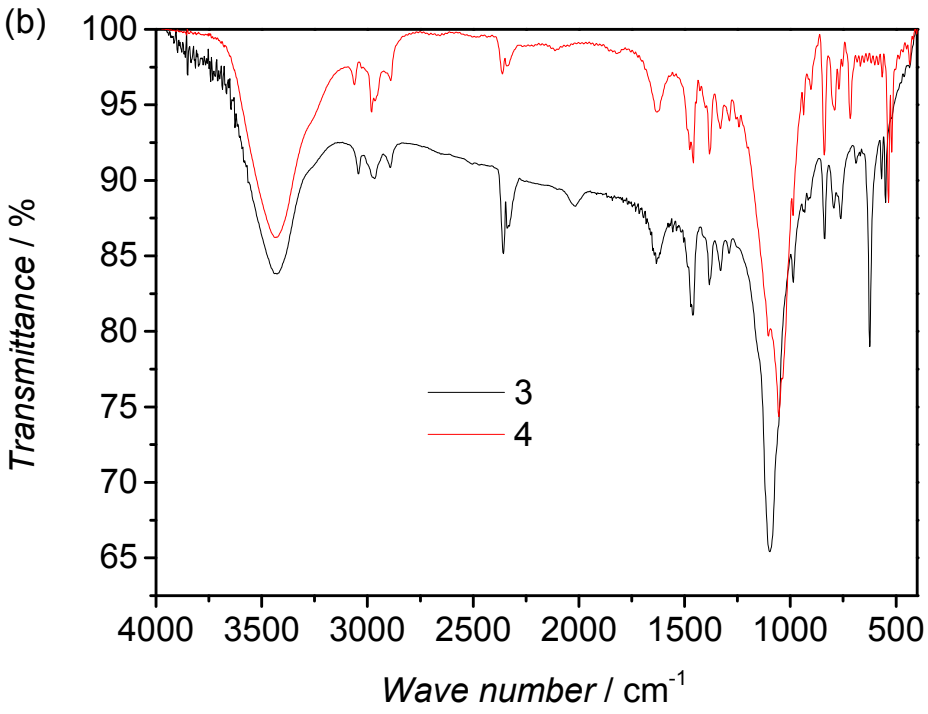
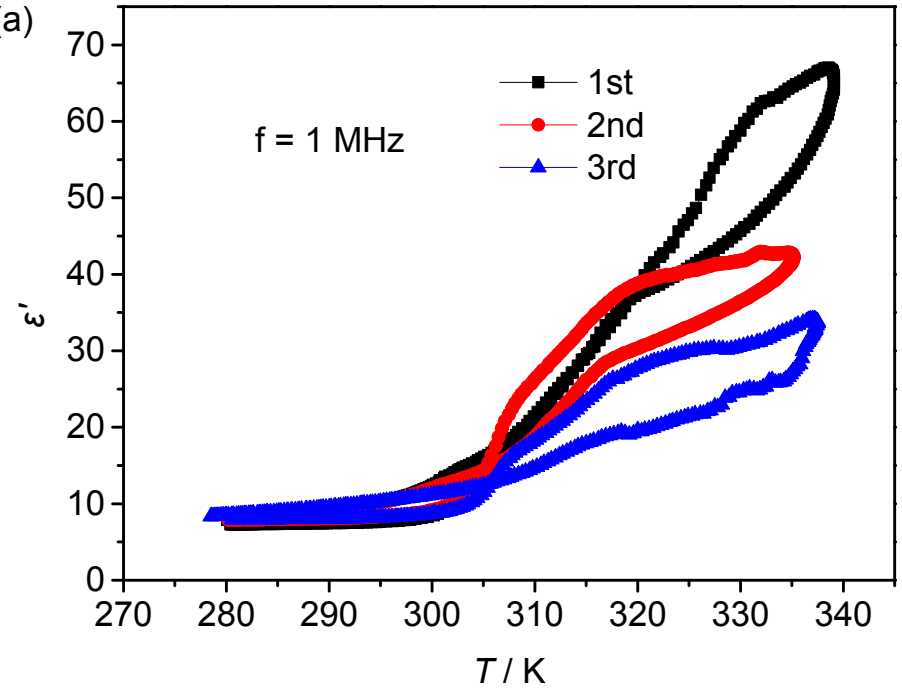


Figure S1 IR spectra of (a) 1 and 2 and (b) 3 and 4.



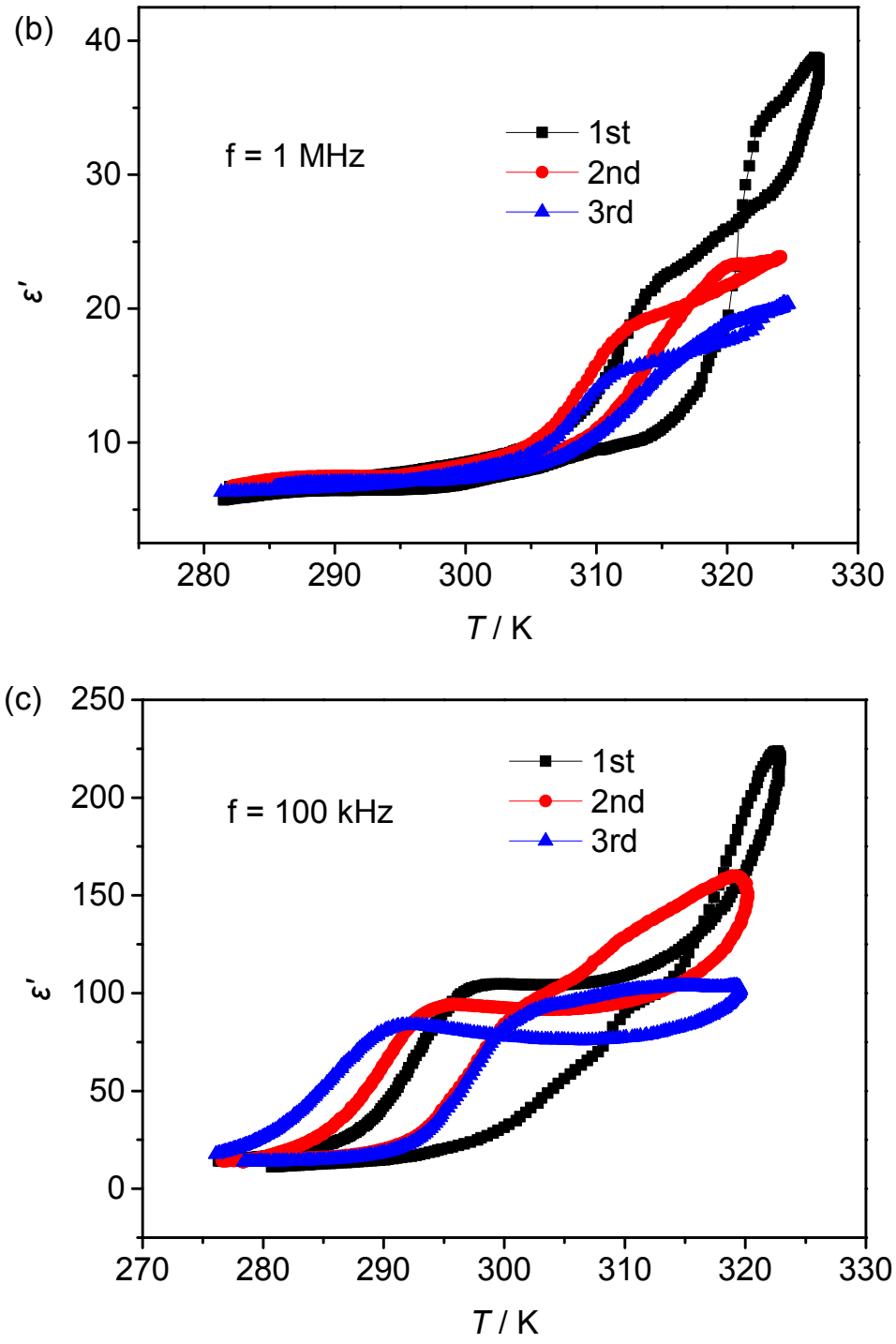


Figure S2 Dielectric spectra of 2(a), 3(b), 4(c).

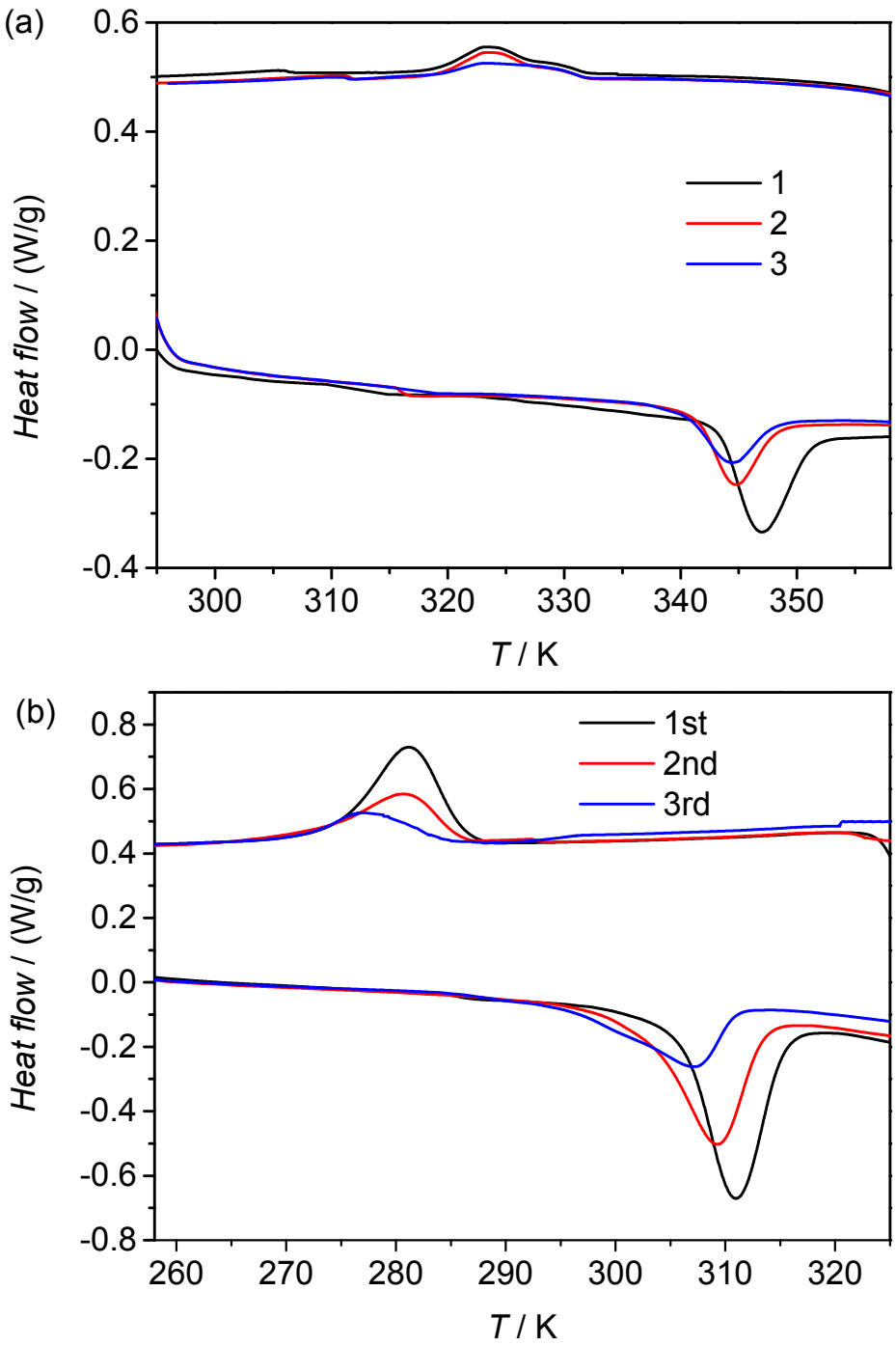
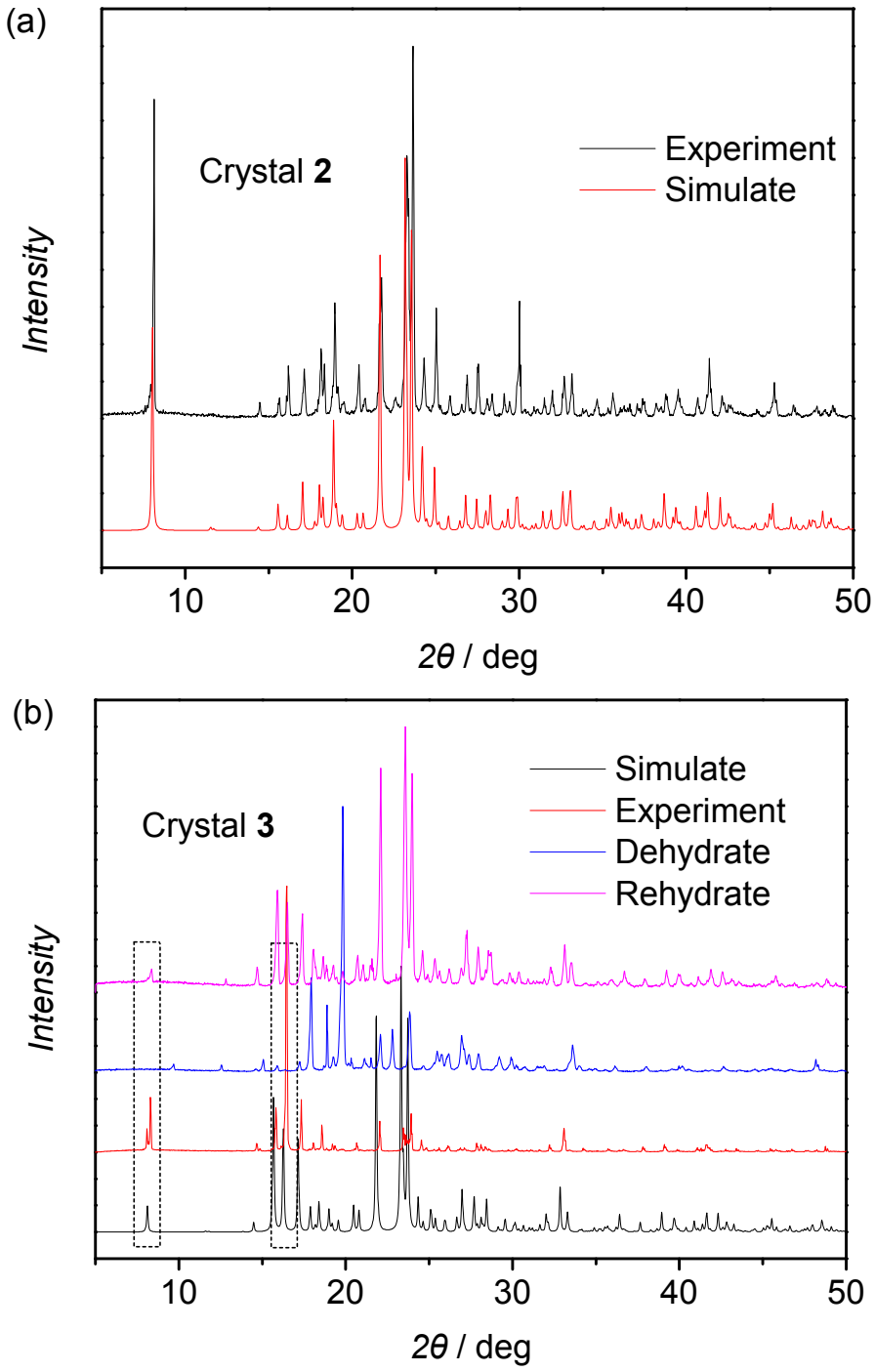


Figure S3 Differential scanning calorimetry (DSC) of 3(a), 4(b).


(a)
Crystal 2
Experiment
Simulate
Intensity
10
20
30
40
50
2θ / deg
(b)
Crystal 3
Simulate
Experiment
Dehydrate
Rehydrate
Intensity
10
20
30
40
50
2θ / deg

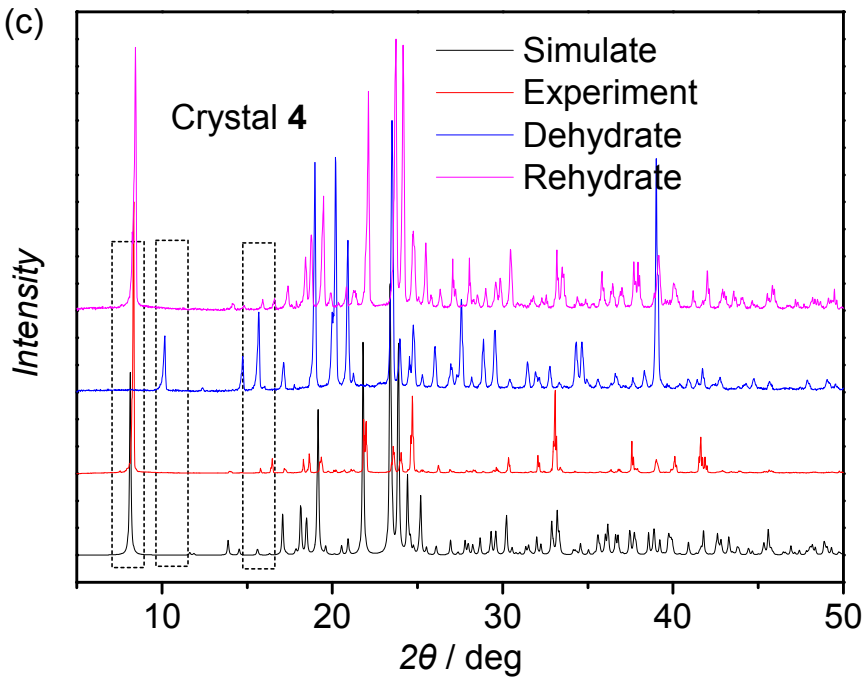
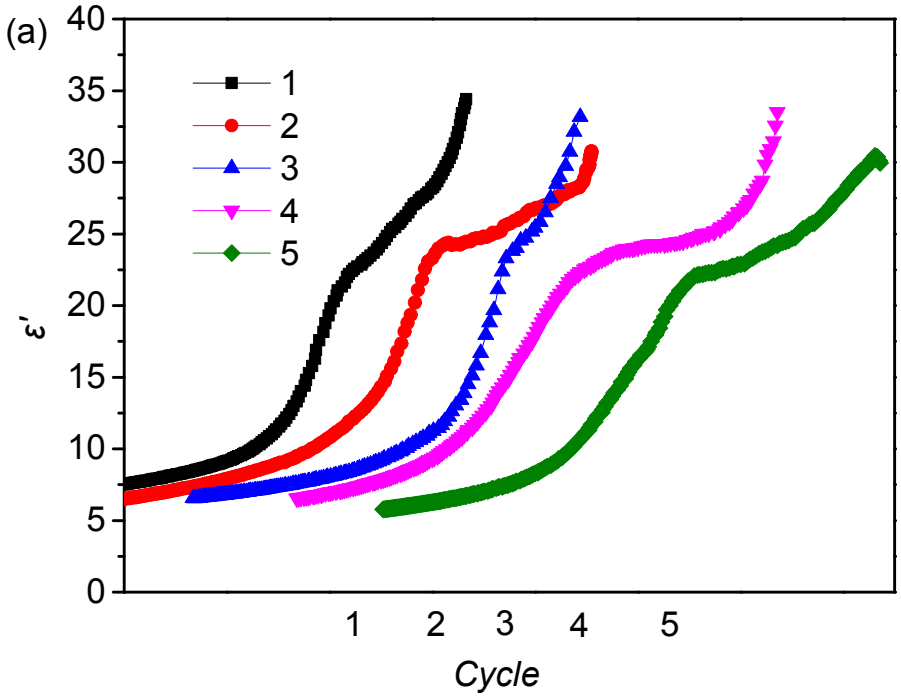


Figure S4 Powder X-ray diffraction patterns of 2(a), 3(b), 4(c).



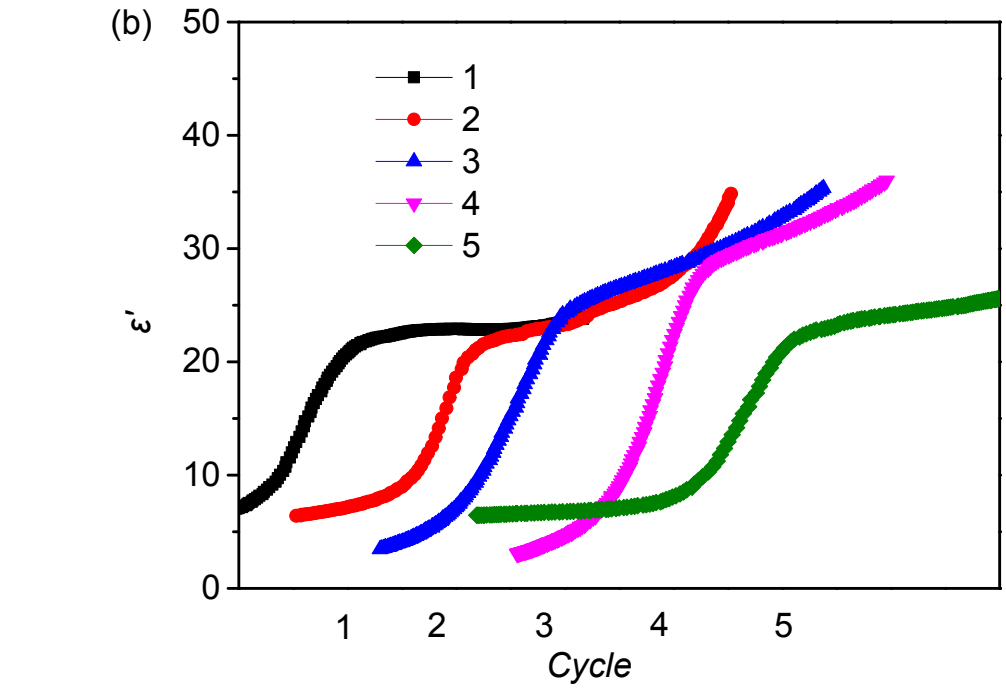
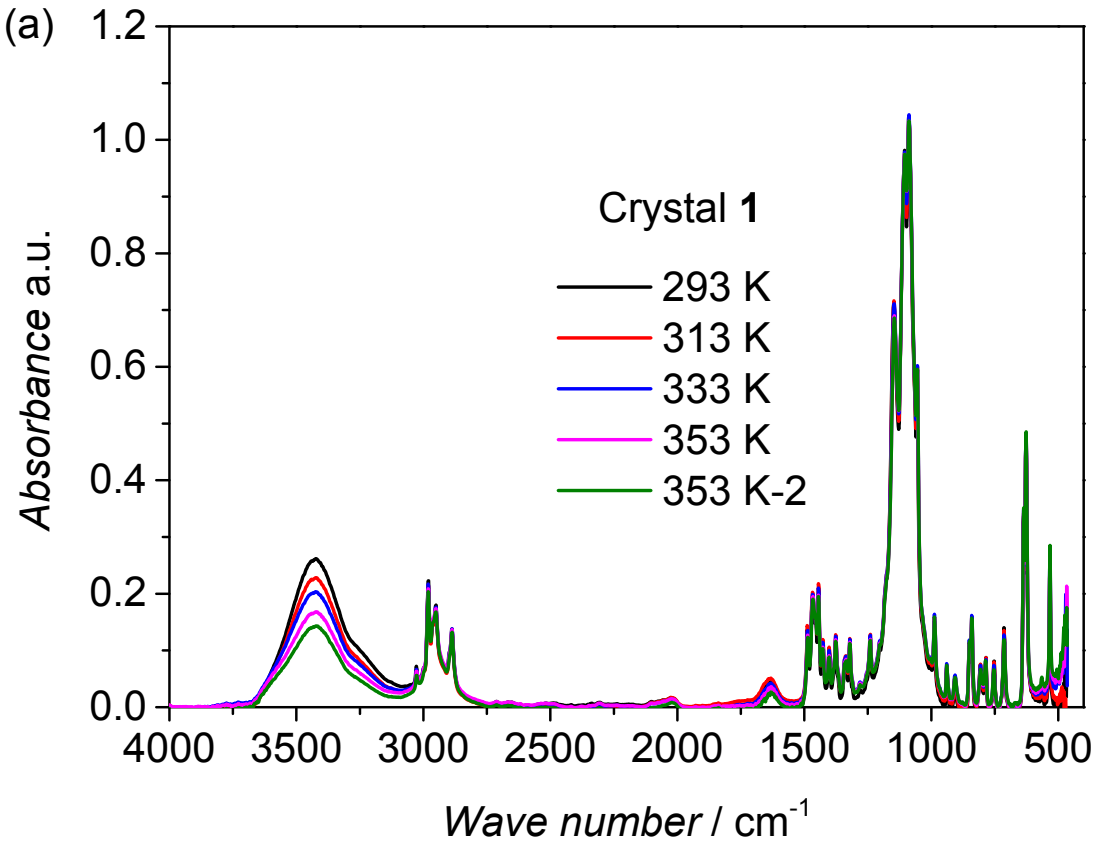


Figure S5 Cycle of dielectric spectra of 3(a), 4(b) at 1MHz upon the cooling.



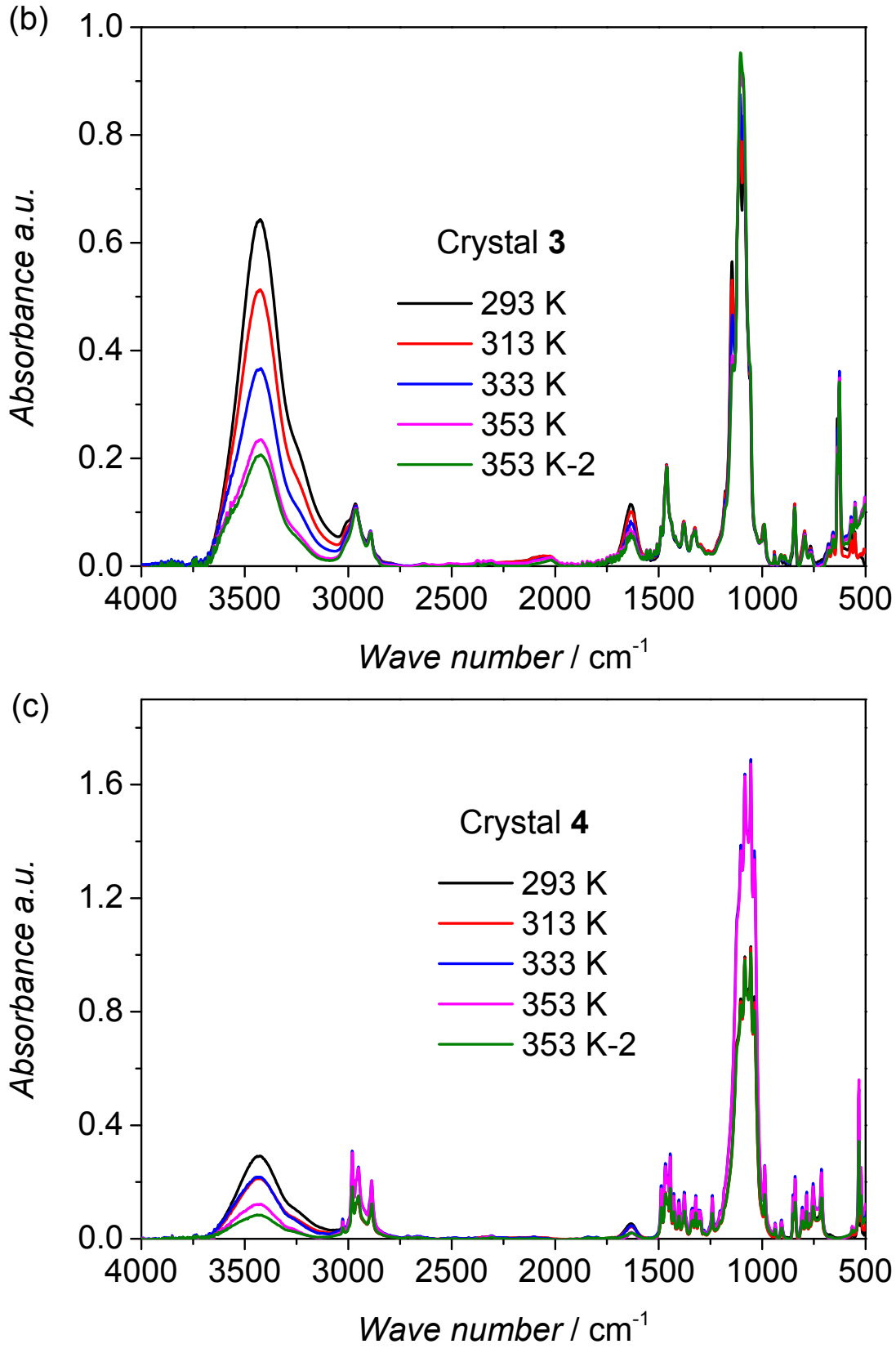


Figure S6 Variable temperatures IR spectra of **1**(a), **3**(b), **4**(c) at 293 K, 313 K, 333 K, and 353 K, 353 K-2 was in-situ temperature data that measured after 5 minutes.