Electronic Supplementary Material (ESI) for New Journal of Chemistry.
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Role of crystallization water molecules on hydrogen-bonded structures and dielectric phase transitions in amino trimethylene phosphonic acid-based crystals

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Table S1. Hydrogen bonds of **1** at 273 K and 113 K.

	D–H ··*A*	*D*–H	H ··*A*	*D* ··*A*	∠*D*–H ··*A*
273 K	N1–H1 ··O9	0.91	2.53	3.016(3)	113.8
	N1–H1 ··O9#2	0.91	1.84	2.653(2)	146.7
	N2–H2C ··O8#4	0.89	1.93	2.791(3)	163.7
	N2–H2D ··O4	0.89	2.04	2.924(3)	172.7
	N2–H2E ··O2#3	0.89	2.24	3.105(3)	164.8
	N3–H3C ··O11#5	0.89	1.96	2.844(3)	175.5
	N3–H3D ··O10#4	0.89	2.04	2.931(3)	174.3
	N3–H3E ··O5	0.89	1.91	2.802(3)	176.9
	O2–H2 ··O1#1	0.85	1.75	2.581(3)	167.9
	O6–H6 ··O3#6	0.81	1.75	2.535(2)	161.5
	O7–H7 ··O4#2	0.87	1.74	2.586(2)	161.7
	O10–H10D ··O1#3	0.82	2.03	2.838(2)	167.6
	O10–H10E ··O8	0.84	2.01	2.842(3)	171.7
	O11–H11D ··O5#2	0.89	1.93	2.810(3)	168.7
	O11–H11E ··O10	0.86	2.05	2.886(3)	165.1
	O12–H12A ··O8	0.85	2.59	3.139(3)	123(2)
	O12–H12A ··O9	0.85	2.076	2.894(4)	161(3)
	O12–H12B ··O6#4	0.85	2.20	2.959(4)	148(4)
113 K	N1–H1 ··O9	0.86	2.49	3.007(2)	118.8
	N1–H1 ··O9#7	0.86	1.92	2.649(2)	141.3
	N2–H2C ··O2	0.91	2.18	3.069(2)	165.3
	N2–H2D ··O8#8	0.91	1.89	2.777(2)	164.3
	N2–H2E ··O4#9	0.91	1.99	2.893(2)	172.1
	N3–H3C ··O10#4	0.91	2.00	2.909(2)	173.8
	N3–H3D ··O5	0.91	1.89	2.795(2)	176.0
	N3–H3E ··O11#3	0.91	1.92	2.826(2)	175.8
	O2–H2 ··O1#10	0.8499	1.73	2.575(2)	172(2)
	O6–H6 ··O3#8	0.834	1.71	2.529(2)	169(3)
	O7–H7 ··O4#7	0.869	1.719	2.573(2)	167(2)
	O10–H10D ··O8#11	0.85	1.982	2.825(2)	166(2)
	O10–H10E ··O1#5	0.85	1.973	2.817(2)	171.8
	O11–H11D ··O5#2	0.85	1.951(3)	2.789(2)	174(2)
	O11–H11E ··O10	0.85	2.016	2.853(2)	168.0
	O12–H12A ··O8#9	0.85	2.59	3.125(3)	122.4(19)
	O12–H12A ··O9#9	0.85	2.034	2.870(3)	167(3)
	O12–H12B ··O6#8	0.85	2.165	2.944(3)	152(3)

Symmetry codes: #1: –x+2, –y, –z+1; #2: –x+2, –y+1, –z+1; #3: x, y+1, z; #4: –x+1, –y+1, –z+1; #5: x, y, z+1; #6: –x+1, –y, –z+1; #7: –x+2, –y+2, –z; #8: –x+1, –y+1, –z; #9: x, y–1, z; #10: –x+2, –y+1, –z; #11: x, y–1, z+1.

Table S2. Hydrogen bonds of 2 at 273 K and 103 K.

	D–H ··*A*	*D*–H	H ··*A*	*D* ··*A*	∠*D*–H ··*A*
273 K	N4–H4C ··O7#3	0.89	1.97	2.805(3)	155.6
	N4–H4B ··O4#4	0.89	1.90	2.773(2)	164.8
	N4–H4A ··O3#4	0.89	1.82	2.694(3)	167.5
	N3–H3E ··O4#6	0.89	1.91	2.783(3)	165.3
	N3–H3D ··O9#5	0.89	1.93	2.808(2)	167.7
	N3–H3C ··O1#5	0.89	1.90	2.754(3)	159.1
	N2–H2E ··O1#4	0.89	1.91	2.727(2)	152.2
	N2–H2D ··O5#3	0.89	1.90	2.761(2)	163.9
	N2–H2C ··O7#3	0.89	1.94	2.793(3)	160.8
	O6–H6 ··O5#2	0.84	1.733	2.572(2)	177(2)
	O8–H8 ··O9#3	0.835	1.696	2.530(3)	176(3)
	O2–H2 ··O2#1	1.23	1.23	2.460(3)	180.0
	O10–H10F ··O1#4	0.884	2.161	3.036(3)	171(5)
	O10–H10E ··O7#3	0.886	2.101	2.954(3)	161(4)
	O10–H10D ··O4#4	0.890	2.076	2.963(2)	174(4)
103 K	N4–H4C ··O3#7	0.89	1.90	2.725(2)	152.5
	N4–H4B ··O5#9	0.89	1.90	2.760(2)	162.5
	N4–H4A ··O9#9	0.89	1.92	2.782(2)	161.2
	N3–H3C ··O7#11	0.89	1.93	2.807(2)	167.3
	N3–H3B ··O3#11	0.89	1.90	2.749(2)	159.6
	N3–H3A ··O4#3	0.89	1.90	2.772(2)	166.8
	N2–H2C ··O4	0.89	1.89	2.762(2)	165.4
	N2–H2B ··O1	0.89	1.83	2.711(2)	168.0
	N2–H2A ··O9#10	0.89	1.97	2.800(2)	154.6
	O6–H6 ··O5#3	0.845	1.727	2.571(2)	176(2)
	O8–H8 ··O7#8	0.836	1.700	2.531(2)	172(2)
	O2–H2 ··O2#7	1.226	1.226	2.453(3)	180.0
	O10–H10F ··O3#7	0.88	2.163	3.040(2)	174(5)
	O10–H10E ··O9#7	0.888	2.074	2.946(2)	167(5)
	O10–H10D ··O4#9	0.886	2.095	2.963(2)	167(4)
	O11–H11D ··O1#4	0.897	1.906	2.787(3)	167(3)

Symmetry codes: #1: –x+1, –y+2, –z+1; #2: –x+2, –y+2, –z; #3: –x+1, –y+1, –z; #4: x, y–1, z; #5: –x+1, –y+1, –z+1; #6: x, y–1, z+1; #7: –x, –y+1, –z+1; #8: –x, –y, –z; #9: x, y, z+1; #10: –x, –y+1, –z; #11: x+1, y, z.

Table S3. Fractional coordinates (10^4) and equivalent temperature factors ($Å^2 \cdot 10^3$) for water molecules in **1** and **2**. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	X	Y	Z	U_{eq}
1 (273 K)				
O (10)	6434(2)	6249(2)	2203(1)	30(1)
O (11)	8473(2)	6312(2)	988(1)	38(1)
O (12)	6447(5)	6183(4)	4914(2)	94(1)

1 (113 K)				
O (10)	6439(2)	1255(2)	7201(1)	14(1)
O (11)	8461(2)	1327(2)	5987(1)	17(1)
O (12)	6464(4)	1199(3)	-86(2)	60(1)
2 (273 K)				
O (10)	5000	0	0	50(1)
O (11A)	9499(13)	1271(12)	4971(13)	173(5)
O (11B)	9457(4)	2230(7)	5036(4)	116(2)
2 (103 K)				
O (10)	0	5000	10000	36(1)
O (11)	5474(2)	2697(2)	4894(2)	63(1)

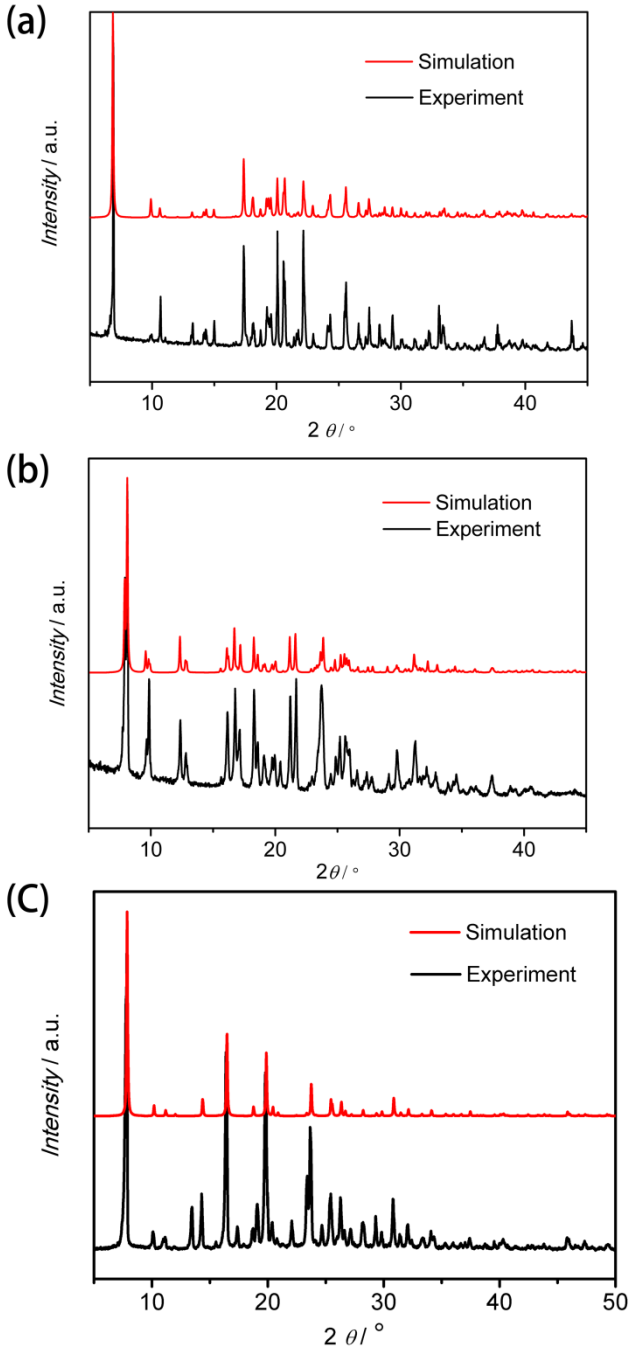

Fig. S1 PXRD patterns of (a) **1**, (b) **2** and (c) **3**.

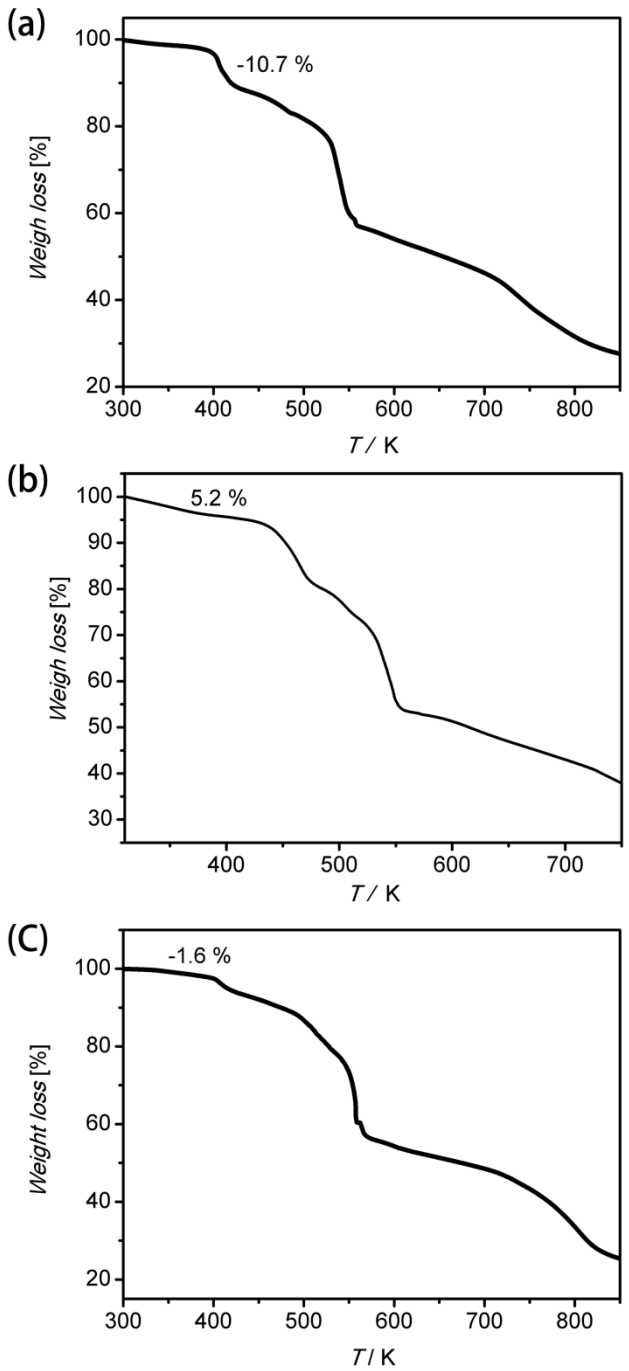

Fig. S2 Thermogravimetric analysis for (a) **1**, (b) **2** and (c) **3**.

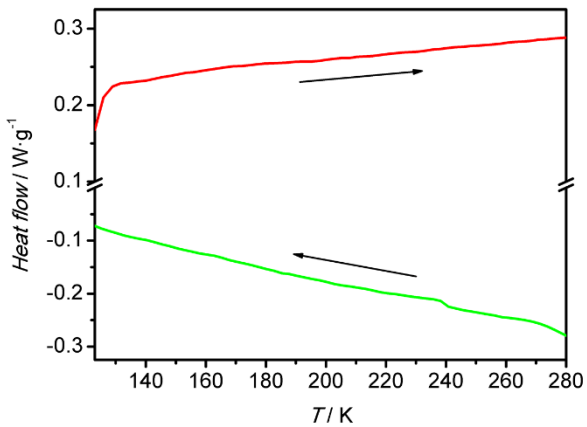

Fig. S3 DSC curves of **1** in the measured temperature range 123−293 K.

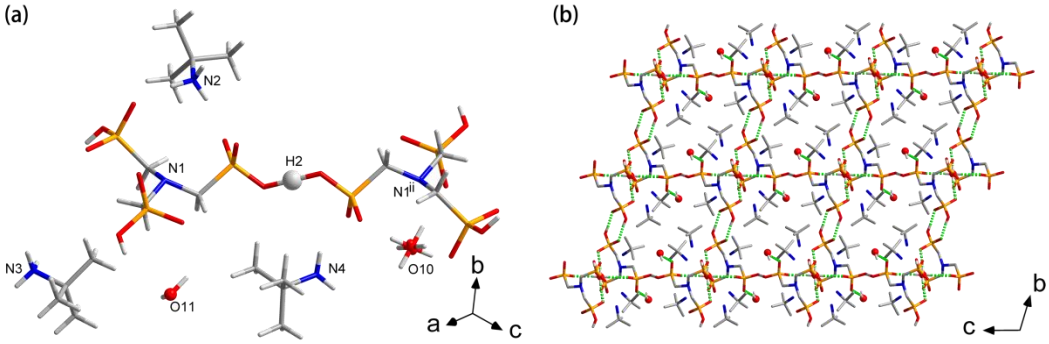

Fig. S4 Asymmetric unit structure of **2** (a) in the LTP and (b) hydrogen-bonded networks along the a axis in the LTP. Symmetry code: (ii): −x, 1−y, 1−z.

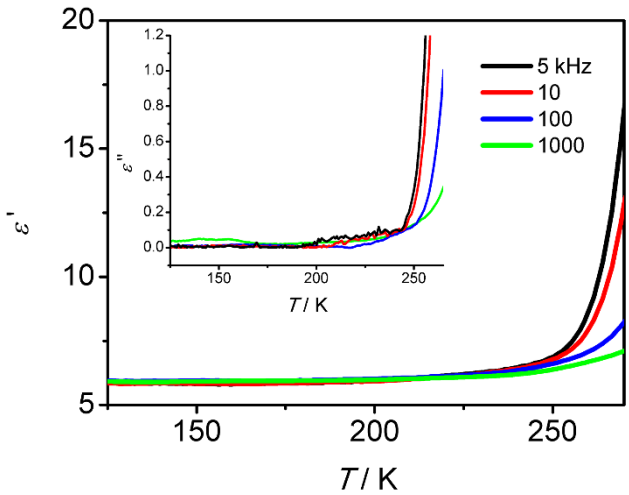

Fig. S5 Temperature-dependence of the real part of the dielectric constant of **2** at selected frequencies on cooling. Inset: imaginary part ε'' in a cooling run.