Synthesis, crystal structure and disorder-order phase transition of a new diamine templated metal sulfate $(C_3H_{12}N_2)_2[Cu(H_2O)_4(SO_4)_2](HSO_4)_2$

Chun-Hong Chen, Rong Mu, Li Zhang, Guan-Cheng Xu*

Key Laboratory of Energy Materials Chemistry (Xinjiang University), Ministry of Education. Key Laboratory of Advanced Functional Materials, Autonomous Region. Institute of Applied Chemistry, Xinjiang University, Urumqi, 830046 Xinjiang, PR China.

Table S1 Selected bond lengths (Å) and bond angles (°) for compound **1** at 293 K and 100 K

293 K			
Cu1−O4	1.997(3)	Cu1−O5	1.941(3)
Cu1−O6	2.469(4)		
O5A−Cu1−O5	180.00(2)	O4A−Cu1−O4	180.00
O5A−Cu1−O4A	92.25(1)	O4−Cu1−O6A	87.69(2)
O5−Cu1−O4A	87.75(1)	O4A−Cu1−O6	87.69(2)
O5A−Cu1−O4	87.75(1)	O4A−Cu1−O6A	92.31(2)
O5−Cu1−O4	92.25(1)	O5−Cu1−O6	88.86(1)
O5A−Cu1−O6A	88.86(1)	O5−Cu1−O6A	91.15(1)
O6−Cu1−O6A	180.00	S1−O4−Cu1	136.24(2)
Cu1−O5−H5A	118.00(4)	Cu1−O5−H5B	112.00(4)

Symmetry transformations used to generate equivalent atoms: A: -x+1, -y+1, -z.

100 K			
Cu1−O4	1.997(1)	Cu1−O5	2.442(5)
Cu1−O6	1.949(1)	Cu2−O14	1.997(1)
Cu2−O15	2.472(2)	Cu2−O16	1.948(1)
O4−Cu1−O4A	180.00	O6−Cu1−O4	92.25(6)
O6−Cu1−O4A	87.75(6)	O6A−Cu1−O4	87.75(6)
O6A−Cu1−O4A	92.25(6)	O6−Cu1−O6A	180.00
O14B−Cu2−O14	180.00	O16B−Cu2−O14B	92.87(6)
O16B−Cu2−O16	180.00	O16−Cu2−O14B	87.13(6)
O16−Cu2−O14	92.87(6)	O16B−Cu2−O14	87.13(6)
S2−O14−Cu2	136.03(8)	S1−O4−Cu1	135.30(8)
Cu1−O6−H6A	120.50	Cu2−O16−H16A	120.30
Cu1−O6−H6B	110.80	Cu2−O16−H16B	112.80

Symmetry transformations used to generate equivalent atoms: A: -x+1, -y, -z+1; B: -x, -y+1, -z.

Table S2 Hydrogen bonds of compound **1** at 293 K and 100 K.

293 K

D−H···A	d(D−H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (°)
N2−H2WC···O8	0.87(4)	2.04(5)	2.872(7)	160(6)
N2−H2WB···O1[a]	0.86(4)	2.10(6)	2.923(7)	161(6)
N2−H2WA···O2[b]	0.87(6)	2.51(8)	3.079(7)	124(6)
N2−H2WA···O10[c]	0.87(6)	2.11(6)	2.865(7)	145(7)
O5−H5A···O8[c]	0.86(6)	1.89(5)	2.737(5)	166(5)
O5−H5B···O2	0.86(7)	1.85(7)	2.636(6)	151(6)
O6−H6A···O7[d]	0.87(5)	1.91(4)	2.772(5)	173(9)
O6−H6B···O1[e]	0.86(5)	1.97(5)	2.827(6)	177(9)
N1− H1WC···O3[f]	0.87(4)	2.03(4)	2.865(6)	160(7)
N1−H1WB···O2	0.87(6)	2.24(6)	2.984(6)	143(7)
N1− H1WB···O10[g]	0.87(6)	2.40(7)	3.065(6)	133(6)
O9− H9A···O3[d]	0.82	1.79	2.610(5)	173.00
N1−H1WA···O6[h]	0.87(6)	2.05(6)	2.885(6)	161(6)

Symmetry transformations used to generate equivalent atoms: a = x, y, 1+z; b = 2-x, 1-y, 1-z; c = 1-x, 1-y, 1-z; d = 1-x, 1-y, -z; e = 2-x, 1-y, -z; f = 1-x, -y, -z; g = 1+x, y, z; h = x, -1+y, z.

100 K

D−H···A	d(D−H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (°)
N4−H1···O7[a]	0.87	1.99	2.839(2)	165
N4−H2···O20[a]	0.86	2.07	2.839(2)	147
N4−H3···O12	0.87	2.06	2.906(2)	163
N3−H4···O20[b]	0.89	2.29	2.982(2)	134
N3−H4···O3[a]	0.89	2.24	2.959(2)	138
N3−H5···O11[a]	0.89	1.99	2.857(2)	167
O5−H5A···O12[g]	0.85	1.97	2.813(2)	176
O5−H5B···O8	0.84	1.93	2.767(2)	172
N3−H6···O15[c]	0.89	2.02	2.866(2)	159
O6−H6A···O3	0.88	1.84	2.648(2)	153
O6−H6B···O19	0.88	1.88	2.750(2)	171
N2−H7···O19[d]	0.88	2.05	2.887(2)	158
N2−H8···O4[e]	0.88	2.55	3.160(2)	127
N2−H8···O2[e]	0.88	2.15	2.892(2)	142
N2−H8···O12[f]	0.88	2.60	3.191(2)	126
N2−H9···O10[d]	0.88	2.19	2.925(2)	140
N2−H9···O13[f]	0.88	2.28	2.975(2)	136
O9−H9A···O11	0.90	1.72	2.620(2)	176
N1−H10···O13	0.89	2.21	2.949(2)	140
N1−H10···O10[g]	0.89	2.41	3.119(2)	136
N1−H11···O1	0.89	2.03	2.874(2)	158
N1−H12···O5	0.89	2.00	2.868(2)	164
O15−H15A···O2[b]	0.87	1.99	2.849(2)	168
O15−H15B···O17[a]	0.88	1.89	2.772(2)	177
O16−H16A···O13	0.84	1.86	2.634(2)	152
O16−H16B···O7[d]	0.85	1.90	2.733(2)	167
O18−H18A···O1[c]	0.89	1.72	2.606(2)	178
C2−H2A···O10[g]	0.99	2.52	3.255(3)	131
C2−H2B···O17[d]	0.99	2.54	3.473(3)	157
C6−H6C···O20[b]	0.99	2.59	3.258(2)	124

Symmetry transformations used to generate equivalent atoms: a = -x, 1-y, 1-z; b = x, 1+y, z; c = x, y, 1+z; d = x, y, -1+z; e = 1-x, -y, -z; f = 1-x, 1-y, -z; g = 1-x, 1-y, 1-z.

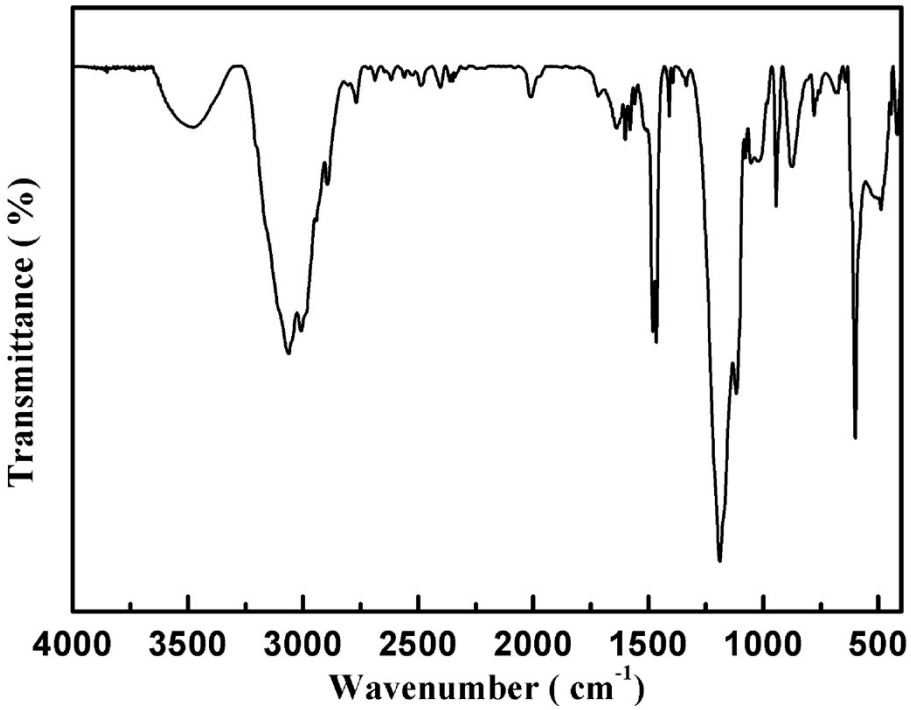

Fig. S1 IR spectrum of compound **1**.

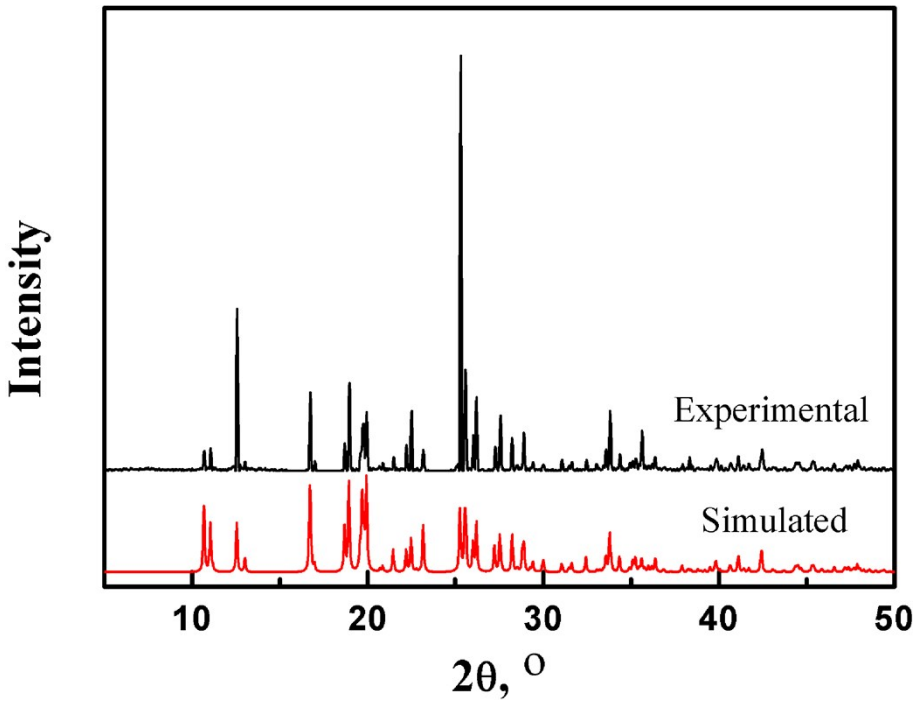

Fig. S2 PXRD pattern of compound **1**.

The result of thermogravimetric (TG) measurement for compound **1** is illustrated in Fig. S3, showing that it remains stable up to about 345 K.

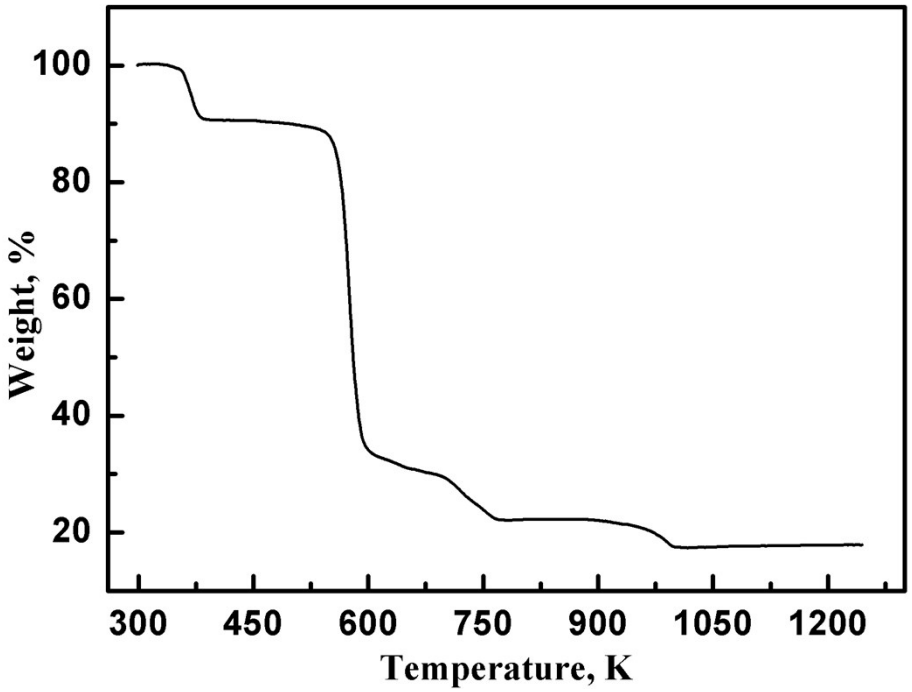

Fig. S3 TG curve of compound **1**.

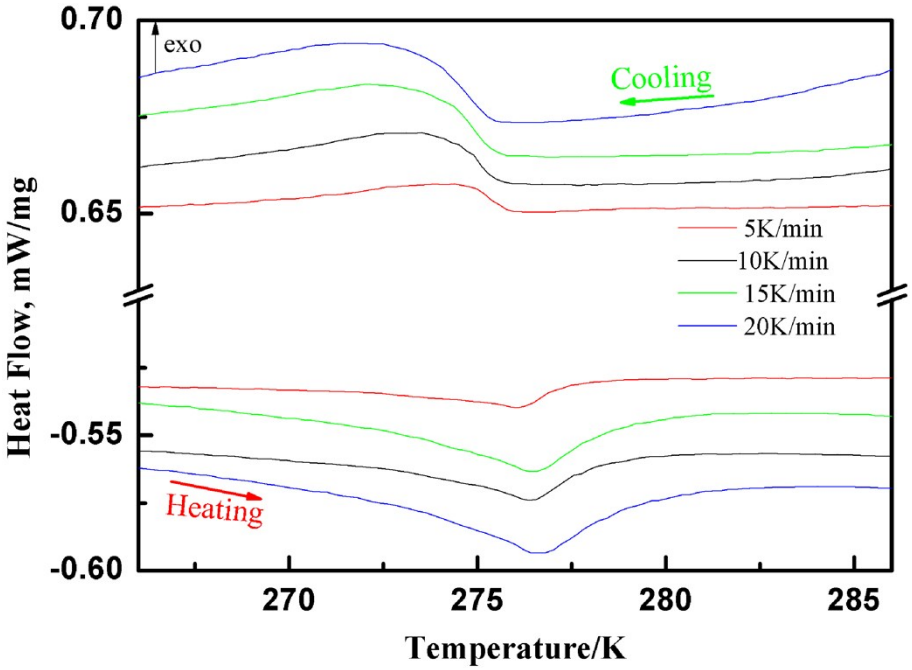

Fig. S4 DSC curves of compound **1** obtained in a heating-cooling mode at 5 K/min, 10 K/min, 15 K/min and 20 K/min, respectively.

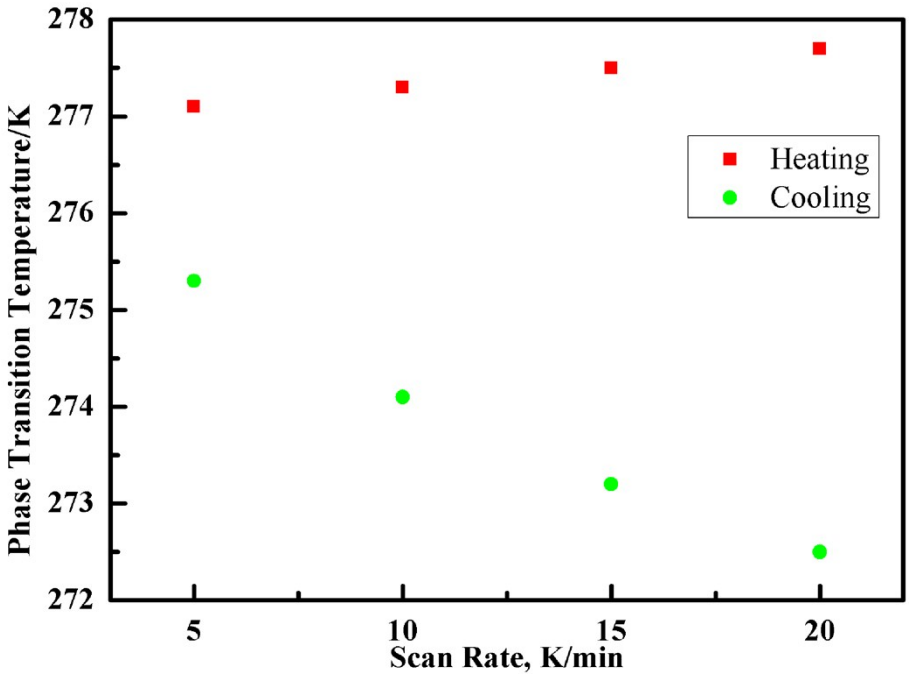

Fig. S5 Phase transition temperatures of compound **1** obtained in a heating-cooling mode at 5 K/min, 10 K/min, 15 K/min and 20 K/min, respectively.

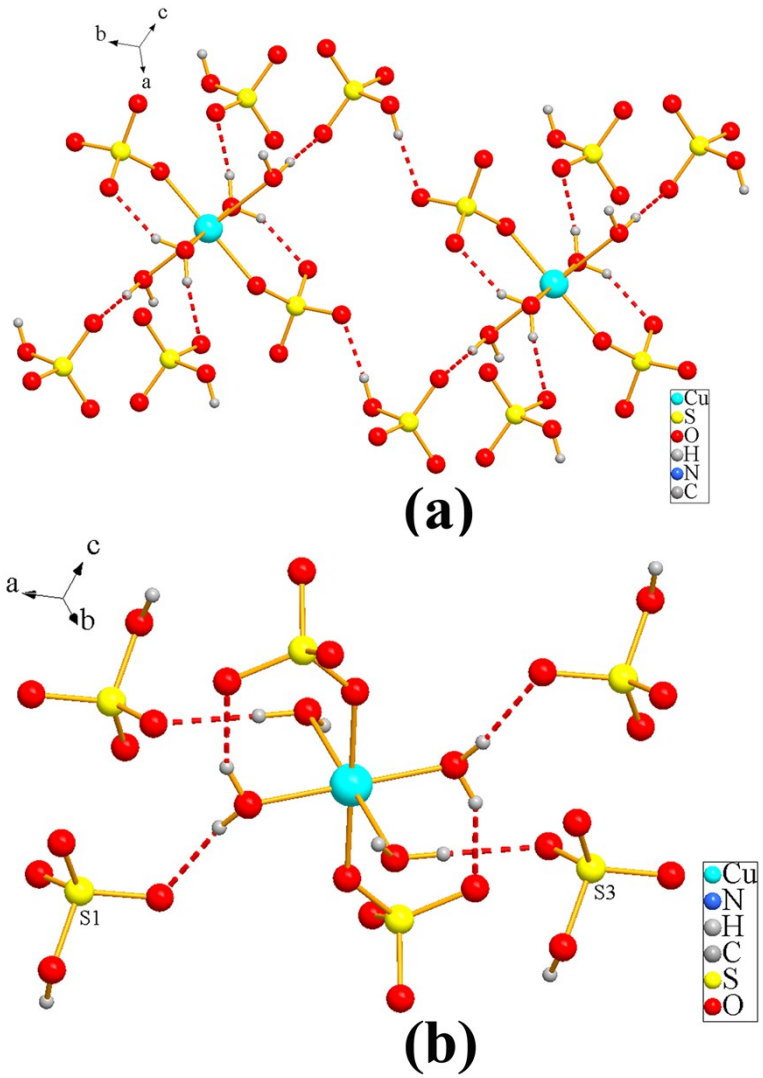

Fig. S6 Neighboring bisulfates in the environment of $[Cu(H_2O)_4(SO_4)_2]$ in compound **1** at (a) 293 K and (b) 100 K.

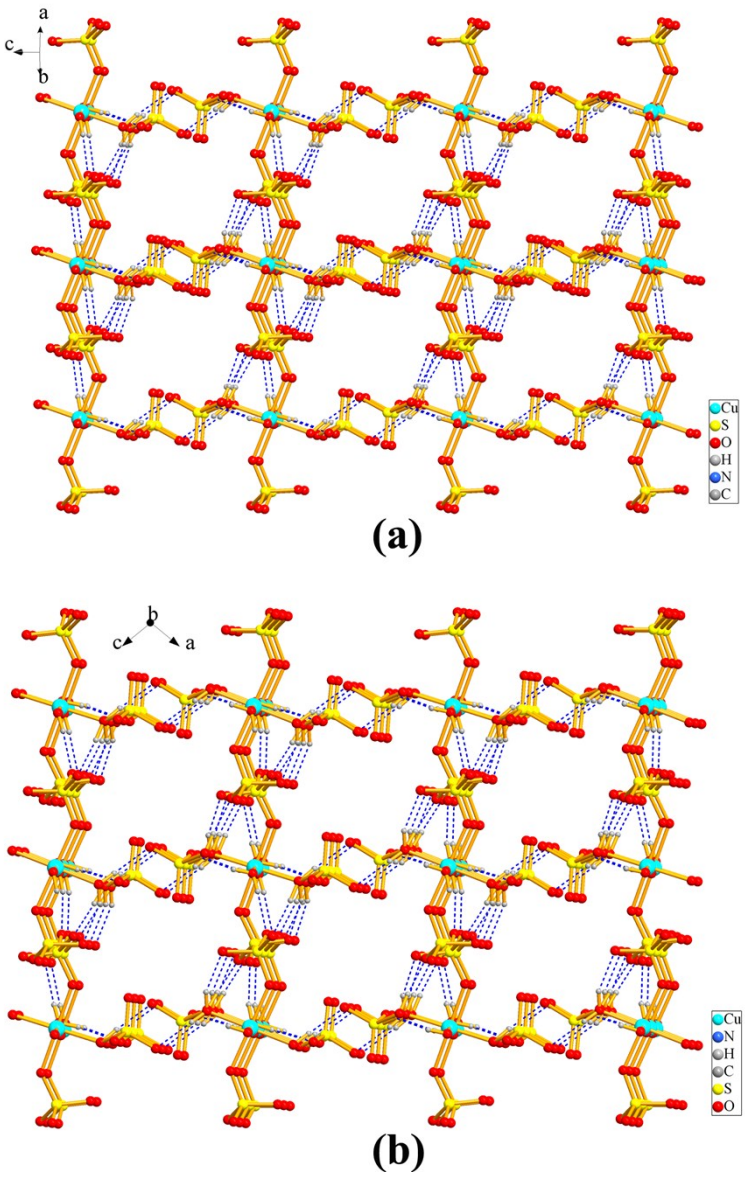

Fig. S7 $[Cu(H_2O)_4(SO_4)_2]^{2-}$ and HSO_4^- anions of compound **1** are linked by O−H···O hydrogen bonds to afford a 3D framework at (a) 293 K and (b) 100 K.

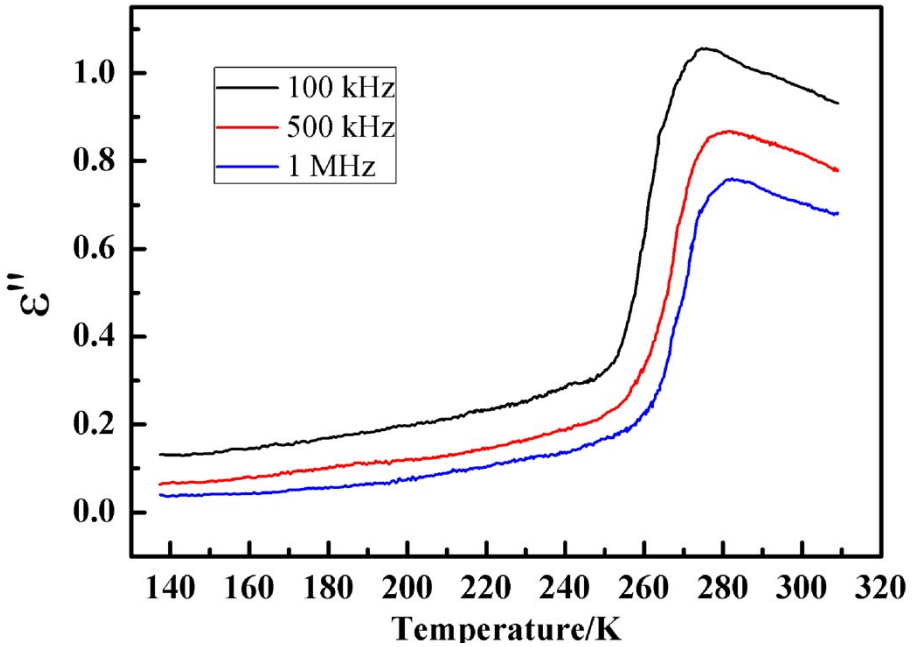

Fig. S8 Temperature dependence of the imaginary part ε″ of dielectric permittivity for compound **1** at different frequencies.