Supporting Information for

Phase Transition and Negative Thermal Expansion in a Guanidinium Magnesium-Hypophosphite Hybrid Perovskites

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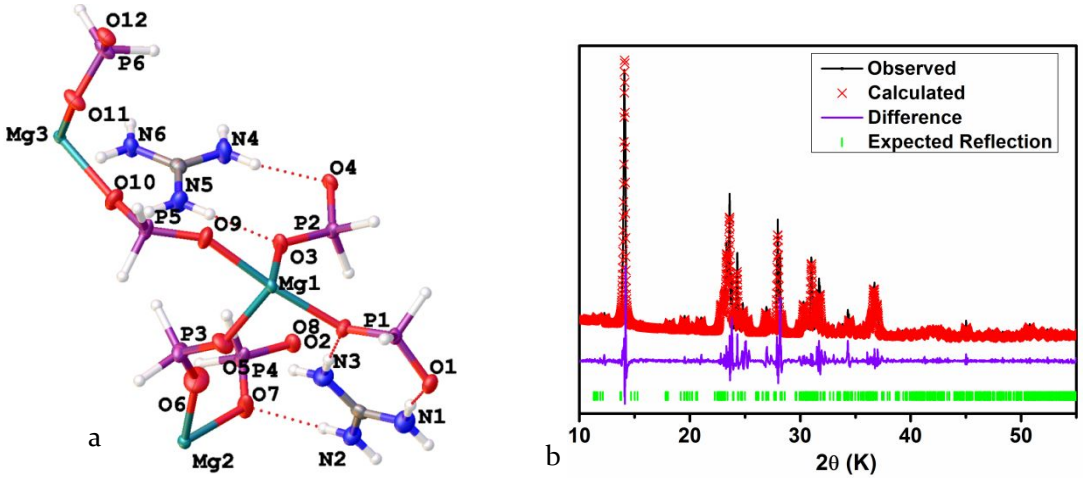

Figure S1. (a) The unit of [Gua]Mg(H_2POO)$_3$ at 290 K. (b) Powder XRD patterns for the as-prepared bulk sample of [Gua]Mg(H_2POO)$_3$ refined by *Le-Bail* method. The black line, red symbol and the purple continuous lines are respectively the experimental, calculated and difference profiles. The vertical markers indicate the expected Bragg reflection.

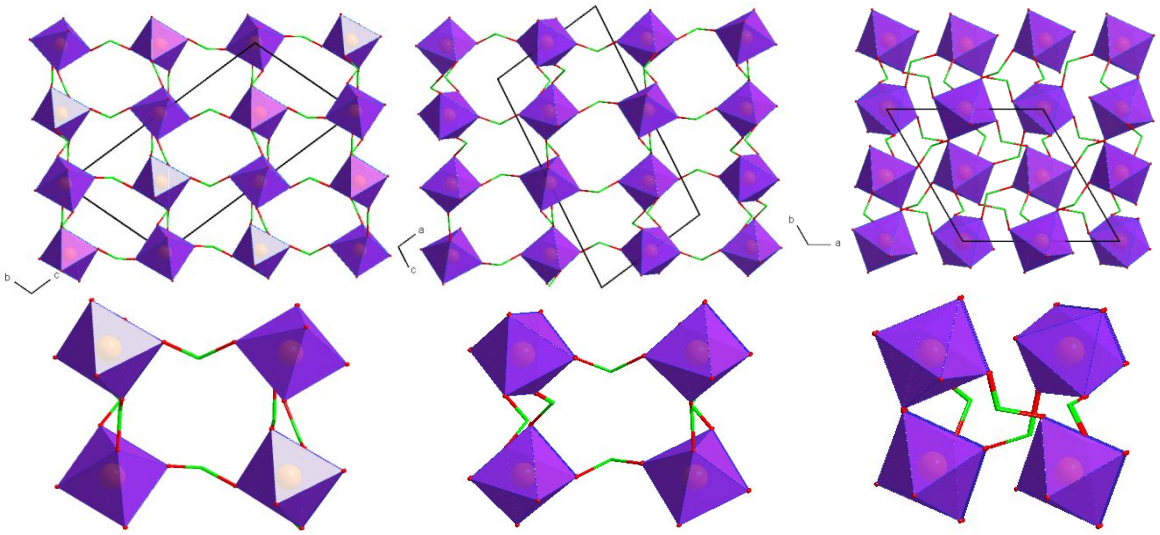

Figure S2. Octahedral layer tilts of [Gua][$Mg(H_2POO)_3$] viewed normal to the three pseudo-cubic perovskite axes. Single 4 * 4 octahedral layers and stacked 2 * 2 layers viewed normal to the three pseudo-cubic perovskite axes. The 4 * 4 layers show the in-plane tilt/shift pattern and the 2 * 2 *4 stacks show the in-axis tilting.

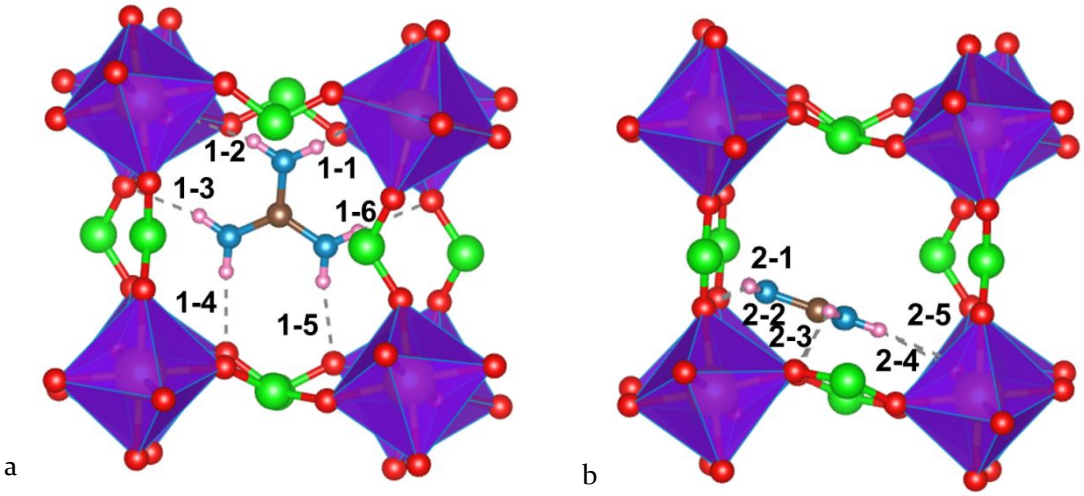

Figure S3. The hydrogen bonds in the frameworks 1 and 2 of [Gua]$Mg(H_2POO)_3$ at 290 K.

Table S1. Crystallographic data for $GuaMg(H_2POO)_3$ at different temperatures.

[Gua]Mg(H_2POO)$_3$						
Formula	$C_2H_{24}N_6O_{12}P_6Mg_2$					
Fw	558.71					
T, K	200	220	240	260	280	290
crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
space group	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1
a, Å	8.96306(8)	8.96756(8)	8.97224(8)	8.97733(8)	8.98254(9)	8.98497(10)
b, Å	9.07862(7)	9.07834(7)	9.07775(7)	9.07673(7)	9.07534(7)	9.07444(7)
c, Å	15.52776(14)	15.54301(13)	15.56056(14)	15.58040(14)	15.60122(14)	15.61097(16)
α, °	105.5757(7)	105.5756(7)	105.5779(7)	105.5807(7)	105.5844(7)	105.5831(8)
β, °	90.8937(7)	90.9070(7)	90.9202(7)	90.9377(7)	90.9564(7)	90.9628(9)
γ, °	118.5604(9)	118.5514(8)	118.5403(9)	118.5291(8)	118.5167(9)	118.5074(10)
V, Å^3	1053.428(18)	1055.010(17)	1056.741(18)	1058.610(19)	1060.518(18)	1061.453(18)
Z	2	2	2	2	2	2
F(000)	576	576	576	576	576	576
D_c, g/cm^3	1.761	1.759	1.756	1.753	1.750	1.748
μ (Mo K_α), mm^{-1}	5.958	5.949	5.930	5.929	5.918	5.913
T_{min}, T_{max}	0.489, 1	0.51928, 1	0.52258, 1	0.47656, 1	0.50966, 1	0.46227, 1
θ_{min}, θ_{max}, °	5.669, 73.718	5.668, 73.705	5.667, 73.700	5.666, 73.816	5.666, 73.821	5.665, 73.785
no. total reflns.	10521	10573	10530	10546	10598	10572
no. uniq. reflns, R_{int}	4275, 0.0306	4112, 0.0314	4121, 0.0284	4134, 0.0244	4145, 0.0229	4146, 0.0232
no. obs. [I≥2σ(I)]	4073	4092	4107	4119	4129	4129
no. params	305	305	305	305	305	305
[a]*R*1, [b]*wR*2 [I≥2σ(I)]	0.0334, 0.0884	0.0367, 0.0981	0.0367, 0.0979	0.0352, 0.0923	0.0372, 0.0977	0.0376, 0.0977
[a]*R*1, [b]*wR*2 (all data)	0.0338, 0.0887	0.0371, 0.0984	0.0370, 0.0982	0.0355, 0.0925	0.0375, 0.0980	0.0379, 0.0979
GOF on F^2	1.095	1.076	1.094	1.104	1.087	1.083
[c]$\Delta\rho$, e/Å^3	0.717, -0.599	0.891, -0.689	1.046, -0.700	1.177, -0.639	1.267, -0.611	1.342, -0.561
[d]Max. and mean Δ/σ	0.001, 0.000	0.001, 0.000	0.001, 0.000	0.001, 0.000	0.001, 0.000	0.001, 0.000

a. $R1 = \sum||F_o|-|F_c||/\sum|F_o|$; *b*. $wR2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; *c*. Maximum and minimum residual electron density; *d*. Maximum and mean sigma/shift.

Table S1. Crystallographic data for [Gua]Mg(H_2POO)$_3$ at different temperatures, continued.

[Gua]Mg(H_2POO)$_3$					
Formula	$C_2H_{24}N_6O_{12}P_6Mg_2$				
Fw	558.71				
T, K	300	310	320	340	360
crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
space group	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1
a, Å	8.98838(8)	8.99093(8)	8.99336(8)	8.99858(10)	9.00382(15)
b, Å	9.06949(8)	9.06819(8)	9.06691(8)	9.06439(9)	9.06181(12)
c, Å	15.62933(14)	15.64192(14)	15.65427(14)	15.67955(16)	15.7050(2)
α, °	105.5887(8)	105.5955(8)	105.5997(8)	105.6072(9)	105.6168(12)
β, °	90.9969(7)	91.0079(7)	91.0186(8)	91.0437(9)	91.0614(13)
γ, °	118.5040(9)	118.5002(9)	118.4961(9)	118.4883(11)	118.4817(15)
V, Å^3	1062.391(19)	1063.347(18)	1064.299(19)	1066.28(2)	1068.26(3)
Z	2	2	2	2	2
F(000)	576	576	576	576	576
D_c, g/cm^3	1.747	1.745	1.743	1.740	1.737
μ (Cu K_α), mm^{-1}	5.908	5.902	5.897	5.886	5.875
T_{min}, T_{max}	0.47114, 1	0.46627, 1	0.51543, 1	0.59949, 1	0.59817, 1
θ_{min}, θ_{max}, °	5.667, 73.927	5.667, 73.843	5.666, 73.839	5.666, 73.836	5.666, 73.801
no. total reflns.	10574	10583	10597	10557	10482
no. uniq. reflns, R_{int}	4152, 0.0312	4154, 0.0302	4156, 0.0317	4168, 0.0321	4176, 0.0265
no. obs. [I≥2σ(I)]	4127	4125	4130	4143	4151
no. params	305	305	305	305	305
[a]*R*1, [b]*wR*2 [I≥2σ(I)]	0.0417, 0.1078	0.0424, 0.1089	0.0449, 0.1166	0.0461, 0.1194	0.0455, 0.1153
[a]*R*1, [b]*wR*2 (all data)	0.0420, 0.1081	0.0428, 0.1093	0.0454, 0.1170	0.0464, 0.1197	0.0458, 0.1155
GOF on F^2	1.070	1.067	1.045	1.048	1.029
[c]Δρ, e/Å^3	1.406, -0.673	1.397, -0.673	1.352, -0.663	1.233, -0.690	1.028, -0.736
[d]Max. and mean Δ/σ	0.001, 0.000	0.001, 0.000	0.001, 0.000	0.001, 0.000	0.001, 0.000

a. $R1 = \sum||F_o|-|F_c||/\sum|F_o|$; *b*. $wR2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; *c*. Maximum and minimum residual electron density; *d*. Maximum and mean sigma/shift.

Table S2. Hydrogen bonds lengths (Å) in frameworks 1 and 2 under different temperatures.

Framework 1						
T/K	1-1	1-2	1-3	1-4	1-5	1-6
200	2.9890(23)	2.8518(18)	3.0707(23)	2.9137(26)	2.9799(26)	2.9085(21)
220	2.9926(25)	2.8560(19)	3.0797(30)	2.9168(34)	2.9827(34)	2.9124(25)
240	2.9972(27)	2.8596(24)	3.0887(30)	2.9201(34)	2.9849(34)	2.9156(25)
260	3.0021(25)	2.8630(19)	3.0983(35)	2.9225(34)	2.9857(34)	2.9198(25)
280	3.0052(29)	2.8668(24)	3.1109(35)	2.9263(35)	2.9888(35)	2.9252(27)
290	3.0081(29)	2.8687(24)	3.1177(35)	2.9278(35)	2.9895(35)	2.9281(27)
300	3.0155(32)	2.8723(29)	3.1389(35)	2.9309(36)	2.9900(36)	2.9310(32)
310	3.0188(32)	2.8742(29)	3.1500(36)	2.9329(37)	2.9899(36)	2.9348(32)
320	3.0210(33)	2.8766(29)	3.1637(47)	2.9356(43)	2.9921(37)	2.9373(34)
340	3.0284(33)	2.8828(29)	3.1873(47)	2.9417(43)	2.9945(47)	2.9432(35)
360	3.0351(34)	2.8883(29)	3.2154(48)	2.9443(44)	2.9968(47)	2.9465(35)
Framework 2						
T/K	2-1	2-2	2-3	2-4	2-5	2-6
200	2.9001(29)	2.9566(21)	3.0114(24)	2.9155(17)	2.9232(17)	3.0943(30)
220	2.9010(30)	2.9609(23)	3.0150(28)	2.9153(23)	2.9256(22)	3.0980(40)
240	2.9031(30)	2.9633(23)	3.0197(29)	2.9169(23)	2.9269(22)	3.1035(40)
260	2.9036(30)	2.9664(22)	3.0233(27)	2.9210(23)	2.9288(22)	3.1099(40)
280	2.9071(33)	2.9695(26)	3.0265(30)	2.9232(24)	2.9325(23)	3.1130(40)
290	2.9073(33)	2.9712(26)	3.0288(30)	2.9234(24)	2.9335(23)	3.1151(40)
300	2.9111(45)	2.9796(28)	3.0340(34)	2.9264(24)	2.9355(23)	3.1218(47)
310	2.9123(45)	2.9836(29)	3.0363(36)	2.9282(25)	2.9374(23)	3.1273(47)
320	2.9136(45)	2.9872(32)	3.0378(37)	2.9281(25)	2.9398(24)	3.1330(52)
340	2.9167(45)	2.9930(32)	3.0445(39)	2.9288(29)	2.9421(28)	3.1431(55)
360	2.9182(45)	2.9998(32)	3.0528(39)	2.9342(29)	2.9457(28)	3.1530(55)

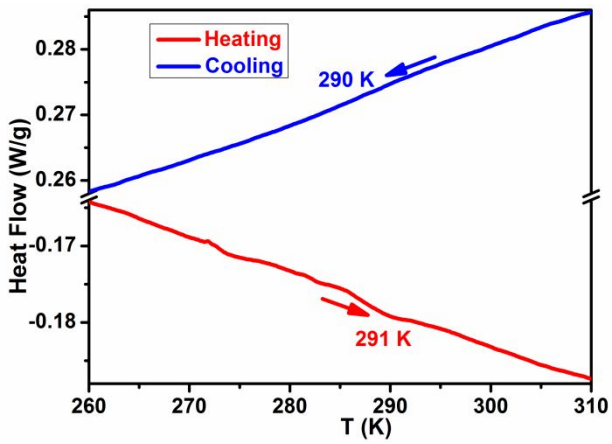

Figure S4. DSC traces for GuaMg(H_2POO)$_3$ in heating and cooling modes.

Table S3. The anisotropic coefficients of thermal expansion (α_l, in 10^{-6} K^{-1}) for $GuaMg(H_2POO)_3$ under different temperatures range.

Expansion coefficients	200−290 K	290−300 K	300−360 K	200−360 K
α_a	31.1(5)	31.7(0)	30.4(2)	31.1(2)
α_b	-7.7(7)	-70.3(0)	-20.5(1)	-17.3(2)
α_c	61.8(15)	127.0(0)	82.3(1)	74.5(27)
α_V	85.4(13)	88.4(0)	92.2(3)	88.6(11)

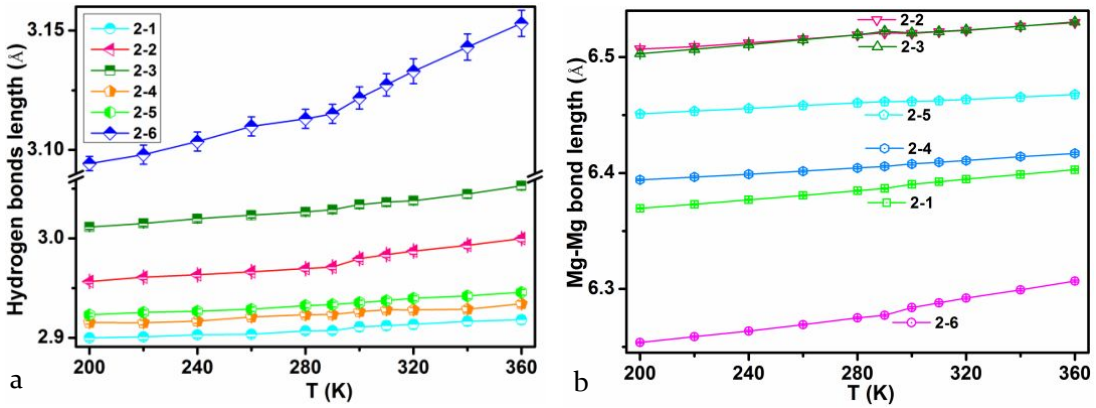

Figure S5. Temperature dependence of hydrogen bonds (a) and Mg-Mg bonds lengths (b) in the framework 2.

Table S4. The Mg···O bond lengths (Å) of frameworks 1 and 2 under different temperatures.

200 K	220 K	240 K	260 K	280 K	290 K	300 K	310 K	320 K	340 K	360 K
2.0547(17)	2.0542(19)	2.0548(19)	2.0553(19)	2.0549(20)	2.0545(20)	2.0534(25)	2.0535(25)	2.0543(26)	2.0546(26)	2.0563(26)
2.0864(16)	2.0880(18)	2.0886(18)	2.0902(18)	2.0916(19)	2.0920(19)	2.0920(20)	2.0929(21)	2.0929(24)	2.0941(24)	2.0957(24)
2.0699(18)	2.0680(19)	2.0688(20)	2.0694(19)	2.0696(20)	2.0701(20)	2.0685(22)	2.0695(22)	2.0687(28)	2.0662(28)	2.0649(28)
2.1069(16)	2.1070(18)	2.1077(18)	2.1092(18)	2.1093(18)	2.1105(19)	2.1094(20)	2.1095(20)	2.1087(21)	2.1093(20)	2.1103(21)
2.0949(17)	2.0959(19)	2.0960(19)	2.0971(19)	2.0971(19)	2.0970(20)	2.0981(20)	2.0990(20)	2.0978(20)	2.0979(20)	2.0993(21)
2.1134(16)	2.1140(18)	2.1148(19)	2.1153(18)	2.1154(19)	2.1155(19)	2.1170(19)	2.1168(19)	2.1165(20)	2.1171(20)	2.1180(26)
2.0836(18)	2.0853(20)	2.0865(20)	2.0880(20)	2.0889(21)	2.0901(21)	2.0887(29)	2.0894(29)	2.0899(29)	2.0918(29)	2.0929(30)
2.0668(13)	2.0654(14)	2.0656(14)	2.0646(14)	2.0645(14)	2.0646(14)	2.0640(19)	2.0637(20)	2.0629(19)	2.0607(20)	2.0588(21)
2.0958(16)	2.0959(18)	2.0965(18)	2.0964(18)	2.0970(19)	2.0980(19)	2.0974(20)	2.0978(20)	2.0988(20)	2.0990(20)	2.0993(20)
2.0453(19)	2.0449(21)	2.0439(22)	2.0421(26)	2.0387(28)	2.0372(28)	2.0346(31)	2.0318(36)	2.0297(37)	2.0258(38)	2.0215(38)
2.1351(10)	2.1362(11)	2.1363(10)	2.1371(11)	2.1390(12)	2.1394(12)	2.1373(12)	2.1381(13)	2.1382(13)	2.1377(15)	2.1382(15)
2.0789(19)	2.0813(20)	2.0829(20)	2.0843(20)	2.0850(21)	2.0860(21)	2.0862(30)	2.0869(30)	2.0881(30)	2.0891(30)	2.0902(30)
2.0864(16)	2.0880(18)	2.0886(18)	2.0902(18)	2.0916(19)	2.0920(19)	2.0920(20)	2.0929(21)	2.0929(24)	2.0941(24)	2.0957(24)
2.0547(17)	2.0542(19)	2.0548(19)	2.0553(19)	2.0549(20)	2.0545(20)	2.0534(25)	2.0535(25)	2.0543(26)	2.0546(26)	2.0563(26)
2.1069(16)	2.1070(18)	2.1077(18)	2.1092(18)	2.1093(18)	2.1105(19)	2.1094(20)	2.1095(20)	2.1087(21)	2.1093(20)	2.1103(21)
2.0699(18)	2.0680(19)	2.0688(20)	2.0694(19)	2.0696(20)	2.0701(20)	2.0685(22)	2.0695(22)	2.0687(28)	2.0662(28)	2.0649(28)
2.1134(20)	2.1140(18)	2.1148(19)	2.1153(18)	2.1154(19)	2.1155(19)	2.1170(19)	2.1168(19)	2.1165(20)	2.1171(20)	2.1180(26)
2.0949(17)	2.0959(19)	2.0960(19)	2.0971(19)	2.0971(19)	2.0970(20)	2.0981(20)	2.099(20)	2.0978(20)	2.0979(20)	2.0993(21)

Table S5. The Mg···Mg bond lengths (Å) of frameworks 1 and 2 under different temperatures.

T/K	**Framework 1**					
200	6.3696(5)	6.5069(7)	6.5030(5)	6.2538(7)	6.4511(7)	6.3941(7)
220	6.3730(6)	6.5090(7)	6.5067(6)	6.2588(7)	6.4534(8)	6.3965(8)
240	6.3769(6)	6.5122(7)	6.5107(6)	6.2637(7)	6.4557(8)	6.3989(8)
260	6.3807(6)	6.5156(7)	6.515(6)	6.2692(7)	6.4583(8)	6.4016(8)
280	6.3848(6)	6.5191(7)	6.5192(6)	6.2751(7)	6.4606(8)	6.4044(8)
290	6.3867(6)	6.5208(8)	6.5223(6)	6.2773(8)	6.4616(8)	6.4057(8)
300	6.3902(7)	6.5204(9)	6.5208(6)	6.2839(9)	6.4618(9)	6.4078(9)
310	6.3924(7)	6.5219(9)	6.5220(6)	6.2880(9)	6.4625(9)	6.4093(9)
320	6.3947(7)	6.5230(9)	6.5233(7)	6.2921(9)	6.4635(10)	6.4108(10)
340	6.3987(7)	6.5267(9)	6.5265(7)	6.2992(9)	6.4656(10)	6.4141(10)
360	6.4028(7)	6.5297(9)	6.5303(7)	6.3068(9)	6.4678(10)	6.4169(10)
Framework 2						
200	6.3696(5)	6.5069(7)	6.5030(5)	6.2538(7)	6.3941(7)	6.4511(7)
220	6.3730(6)	6.5090(7)	6.5067(6)	6.2588(7)	6.3965(8)	6.4534(8)
240	6.3769(6)	6.5122(7)	6.5107(6)	6.2637(7)	6.3989(8)	6.4557(8)
260	6.3807(6)	6.5156(7)	6.515(6)	6.2692(7)	6.4016(8)	6.4583(8)
280	6.3848(6)	6.5191(7)	6.5192(6)	6.2751(7)	6.4044(8)	6.4606(8)
290	6.3867(6)	6.5208(8)	6.5223(6)	6.2773(8)	6.4057(8)	6.4616(8)
300	6.3902(7)	6.5204(9)	6.5208(6)	6.2839(9)	6.4078(9)	6.4618(9)
310	6.3924(7)	6.5219(9)	6.5220(6)	6.2880(9)	6.4093(9)	6.4625(9)
320	6.3947(7)	6.5230(9)	6.5233(7)	6.2921(9)	6.4108(10)	6.4635(10)
340	6.3987(7)	6.5267(9)	6.5265(7)	6.2992(9)	6.4141(10)	6.4656(10)
360	6.4028(7)	6.5297(9)	6.5303(7)	6.3068(9)	6.4169(10)	6.4678(10)

Table S6. The hinge angles (°) in frameworks 1 and 2 under different temperatures.

Framework 1					
T/K	φ1-1	φ1-2	φ1-3=φ1-4	θ1-1	θ1-2=θ1-3=θ1-4
200	89.708(8)	86.374(7)	87.496(8)	91.410(8)	92.504(8)
220	89.720(8)	86.408(8)	87.534(8)	91.403(8)	92.466(8)
240	89.740(8)	86.443(8)	87.571(8)	91.383(8)	92.429(8)
260	89.767(8)	86.484(8)	87.617(8)	91.363(8)	92.383(8)
280	89.792(8)	86.529(8)	87.664(9)	91.340(8)	92.336(8)
290	89.811(8)	86.541(8)	87.688(9)	91.332(8)	92.312(9)
300	89.802(10)	86.634(9)	87.740(10)	91.300(10)	92.261(10)
310	89.813(10)	86.676(9)	87.774(10)	91.280(10)	92.226(10)
320	89.822(10)	86.719(10)	87.810(11)	91.265(10)	92.190(11)
340	89.856(10)	86.789(10)	87.874(11)	91.225(10)	92.126(11)
360	89.892(10)	86.866(10)	87.949(11)	91.188(10)	92.051(11)
Framework 2					
T/K	φ2-1=φ2-2	φ2-3	φ2-4	θ2-1=θ2-2=θ2-3	θ2-4
200	88.590(8)	89.708(8)	86.374(7)	91.410(8)	92.504(8)
220	88.597(8)	89.720(8)	86.408(8)	91.403(9)	92.466(8)
240	88.617(8)	89.740(8)	86.443(8)	91.383(9)	92.429(8)
260	88.637(8)	89.767(8)	86.484(8)	91.363(9)	92.383(8)
280	88.660(8)	89.792(8)	86.529(8)	91.340(9)	92.336(8)
290	88.668(9)	89.811(9)	86.541(8)	91.332(10)	92.312(9)
300	88.700(10)	89.802(10)	86.634(9)	91.300(10)	92.260(10)
310	88.721(10)	89.813(10)	86.676(9)	91.280(10)	92.226(10)
320	88.735(10)	89.820(10)	86.719(10)	91.265(11)	92.190(11)
340	88.775(10)	89.856(10)	86.789(10)	91.225(11)	92.126(11)
360	88.812(10)	89.892(10)	86.866(10)	91.188(11)	92.051(11)

Table S7. The torsion angles (°) of frameworks 1 and 2 under different temperatures.

	Framework 1			**Framework 2**		
T/K	1-1	1-2	1-3	2-1	2-1	2-3
200	24.701(80)	4.242(80)	13.114(77)	16.727(79)	4.507(80)	22.655(79)
220	25.065(94)	4.245(103)	13.208(91)	16.727(93)	4.452(104)	22.800(93)
240	25.428(99)	4.266(104)	13.297(96)	16.754(94)	4.459(104)	22.965(93)
260	25.875(100)	4.279(103)	13.391(91)	16.735(92)	4.386(104)	23.186(93)
280	26.424(111)	4.336(107)	13.527(102)	16.721(100)	4.331(107)	23.388(100)
290	26.718(111)	4.339(107)	13.586(102)	16.697(100)	4.321(107)	23.474(100)
300	27.600(121)	4.111(112)	13.704(112)	16.675(110)	4.123(112)	23.897(118)
310	28.130(126)	4.123(113)	13.829(112)	16.600(117)	4.087(119)	24.100(119)
320	28.721(141)	4.063(130)	13.963(119)	16.542(125)	3.932(125)	24.327(125)
340	29.717(142)	4.063(138)	14.172(125)	16.515(131)	3.727(135)	24.765(132)
360	30.857(143)	4.059(139)	14.333(128)	16.539(131)	3.561(136)	25.266(134)

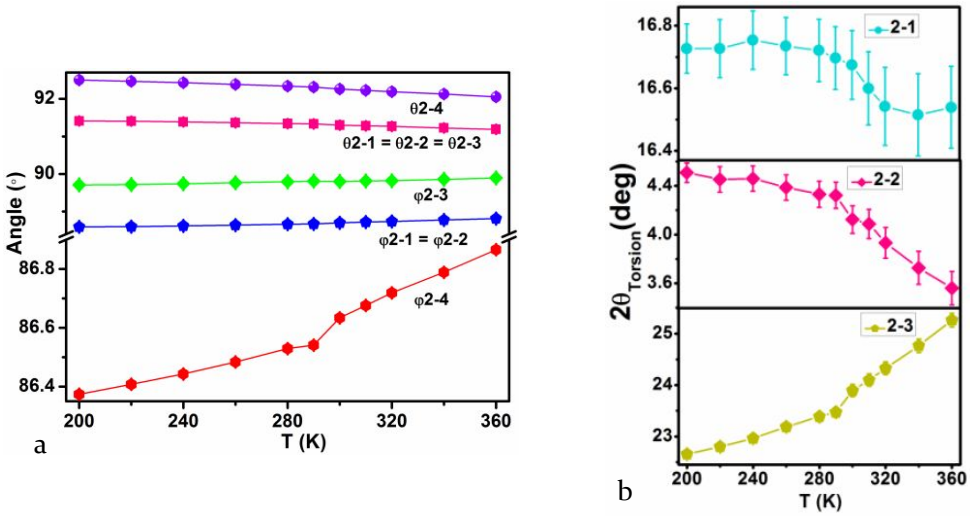

Figure S6. Temperature dependence of $2\theta_{Torsion}$ (a) and hinge angles θ and φ (b) in the framework 2.

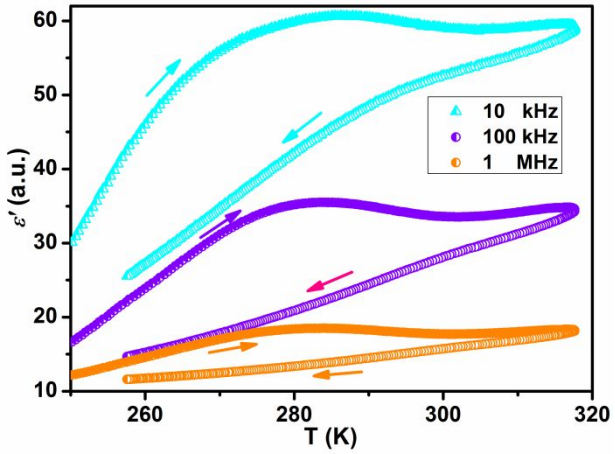

Figure S7. Temperature-variable the real parts (ε′) of dielectric constants in the frequencies range from 10 kHz to 1 MHz of [Gua]Mg(H2POO)3 during heating and cooling processes.

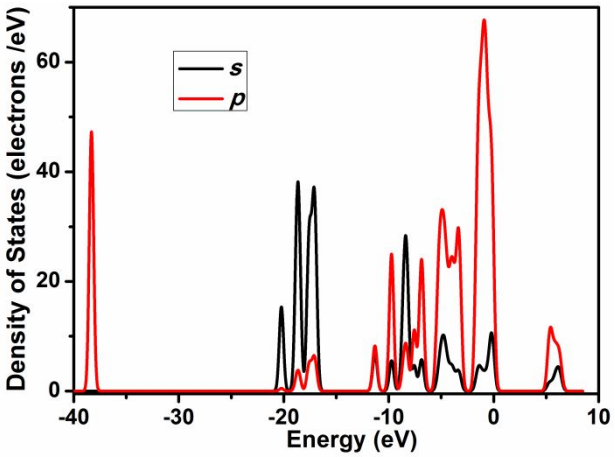

Figure S8. Decomposed DOS of *s*- and *p*-orbitals for [Gua]Mg($H_2POO)_3$.