Supporting information for

Explorations of Second-Order Nonlinear Optical Materials in the Alkaline Earth Barbiturates System: Noncentrosymmetric $Ca(H_3C_4N_2O_3)_2•H_2O$ and Centrosymmetric $Sr(H_5C_8N_4O_5)_2•4H_2O$

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Table S1 Atomic coordinates and equivalent isotropic displacement parameters for $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$.

Atom	x	y	z	U(eq)
Ca1	5000	0	5626.8(11)	19.6(2)
O1	5776.9(16)	809.3(18)	8496(3)	32.9(6)
N3	6216.9(17)	2480(2)	9310(4)	24.7(5)
C4	8290.6(19)	1955(2)	9355(4)	22.2(6)
C5	7990.4(19)	2978(2)	9695(5)	24.3(6)
N6	7497.1(17)	1229(2)	8925(4)	24.3(5)
C7	6461.2(19)	1478(2)	8882(5)	21.0(6)
C9	6941.0(19)	3271(2)	9704(5)	25.0(6)
O0AA	9214.1(13)	1598.7(17)	9438(4)	29.4(5)
O2	6600.4(14)	4170.5(17)	10079(4)	40.2(7)
O1AA	5000	0	2082(7)	102(3)

Table S2 Atomic coordinates and equivalent isotropic displacement parameters for $Sr(H_5C_8N_4O_5)_2 \cdot 4H_2O$

Atom	x	y	z	U(eq)
Sr(1)	2404(1)	6924(1)	4091(1)	47(1)
O(1)	6070(15)	7392(6)	4313(6)	50(3)
O(2)	4770(15)	5822(6)	4426(6)	52(3)
O(3)	1066(15)	8053(4)	4555(5)	40(2)
O(4)	-374(16)	6159(6)	4364(5)	55(3)
O(5)	2193(9)	3624(2)	9015(3)	54(2)
O(6)	2833(9)	5951(2)	9132(3)	51(1)
O(7)	3308(15)	7896(3)	7902(4)	90(3)
O(8)	2676(9)	4712(3)	6735(3)	52(1)
O(9)	2714(10)	7111(3)	822(3)	58(2)
O(10)	2375(9)	4758(2)	660(3)	51(1)
O(11)	2244(8)	2708(2)	2148(3)	47(1)
O(12)	2135(9)	4059(3)	4294(3)	58(2)
O(13)	2280(9)	5962(2)	3055(3)	47(1)
O(14)	2949(10)	6828(3)	5555(3)	62(2)
N(1)	2501(9)	4196(3)	7884(3)	41(1)
N(2)	2579(9)	4790(3)	9038(3)	39(1)
N(3)	2925(12)	6705(3)	7851(4)	55(2)
N(4)	3063(10)	7349(3)	6722(4)	47(2)
N(5)	2118(9)	3393(3)	3208(3)	42(1)
N(6)	2211(9)	4593(3)	3123(4)	42(1)
N(7)	2539(11)	6494(3)	1920(4)	46(2)
N(8)	2561(10)	5927(3)	763(4)	44(2)
C(1)	2408(11)	4173(3)	8659(4)	41(2)
C(2)	2735(11)	5438(3)	8686(4)	38(1)
C(3)	2737(10)	5443(3)	7867(4)	35(1)
C(4)	2651(10)	4801(3)	7454(4)	36(1)
C(5)	2840(10)	6096(3)	7441(5)	40(2)
C(6)	2858(10)	6133(3)	6663(4)	38(2)
C(7)	2983(12)	6767(4)	6259(5)	44(2)
C(8)	3106(15)	7348(4)	7526(4)	55(2)

C(9)	2159(10)	4015(3)	3596(4)	38(2)
C(10)	2209(11)	3312(3)	2418(4)	39(2)
C(11)	2194(10)	3932(3)	1973(4)	37(1)
C(12)	2222(10)	4575(3)	2335(4)	36(1)
C(13)	2319(10)	5248(3)	1922(4)	36(1)
C(14)	2355(11)	5885(3)	2350(4)	37(2)
C(15)	2419(10)	5266(3)	1101(4)	39(2)
C(16)	2620(12)	6547(3)	1147(4)	44(2)

Table S3 Bond lengths (Å) for $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$.

Ca1-O1#1	2.426(3)	N3-C7	1.341(5)
Ca1-O1	2.426(3)	N3-C9	1.391(4)
Ca1-O0AA#2	2.404(4)	C4-C5	1.373(5)
Ca1-O0AA#3	2.404(4)	C4-N6	1.400(4)
Ca1-O2#4	2.330(3)	C4-O0AA	1.265(3)
Ca1-O2#5	2.330(3)	C5-C9	1.391(4)
Ca1-O1AA	2.423(6)	N6-C7	1.361(4)
O1-C7	1.246(4)	C9-O2	1.247(4)

#1 1-X,-Y,+Z; #2 3/2-X,+Y,-1/2+Z; #3 -1/2+X,-Y,-1/2+Z;
#4 1-X,1/2-Y,-1/2+Z; #5 +X,-1/2+Y,-1/2+Z

Table S4 Bond lengths (Å) for $Sr(H_5C_8N_4O_5)_2 \cdot 4H_2O$.

Sr(1)-O(1)	2.605(10)	N(2)-C(1)	1.350(9)
Sr(1)-O(2)	2.660(10)	N(2)-C(2)	1.391(8)
Sr(1)-O(3)	2.514(7)	N(3)-H(3)	0.8600
Sr(1)-O(4)	2.471(8)	N(3)-C(5)	1.361(9)
Sr(1)-O(7)#1	3.225(9)	N(3)-C(8)	1.367(9)
Sr(1)-O(11)#2	2.651(5)	N(4)-H(4)	0.8600
Sr(1)-O(13)	2.560(5)	N(4)-C(7)	1.369(9)
Sr(1)-O(14)	2.510(6)	N(4)-C(8)	1.384(9)
O(1)-H(1A)	0.8858	N(5)-H(5)	0.8600
O(1)-H(1B)	0.8858	N(5)-C(9)	1.365(9)
O(2)-H(2A)	0.8898	N(5)-C(10)	1.382(9)
O(2)-H(2B)	0.8895	N(6)-H(6)	0.8600
O(3)-H(3A)	0.9432	N(6)-C(9)	1.378(9)
O(3)-H(3B)	0.9397	N(6)-C(12)	1.361(9)
O(4)-H(4A)	1.0157	N(7)-H(7)	0.8600
O(4)-H(4B)	1.0219	N(7)-C(14)	1.398(8)
O(5)-C(1)	1.236(8)	N(7)-C(16)	1.347(9)
O(6)-C(2)	1.244(8)	N(8)-H(8)	0.8600
O(7)-Sr(1)#3	3.225(9)	N(8)-C(15)	1.404(9)
O(7)-C(8)	1.232(9)	N(8)-C(16)	1.358(8)
O(8)-C(4)	1.254(8)	C(2)-C(3)	1.414(10)
O(9)-C(16)	1.223(9)	C(3)-C(4)	1.420(9)
O(10)-C(15)	1.232(8)	C(3)-C(5)	1.456(9)
O(11)-Sr(1)#4	2.651(5)	C(5)-C(6)	1.347(11)
O(11)-C(10)	1.249(8)	C(6)-H(6A)	0.9300
O(12)-C(9)	1.211(9)	C(6)-C(7)	1.409(9)

O(13)-C(14)	1.234(8)	C(10)-C(11)	1.412(9)
O(14)-C(7)	1.216(10)	C(11)-H(11)	0.9300
N(1)-H(1)	0.8600	C(11)-C(12)	1.380(9)
N(1)-C(1)	1.347(9)	C(12)-C(13)	1.478(9)
N(1)-C(4)	1.387(9)	C(13)-C(14)	1.425(9)
N(2)-H(2)	0.8600	C(13)-C(15)	1.427(10)

#1 x-1/2,-y+3/2,z-1/2; #2 -x+1/2,y+1/2,-z+1/2
#3 x+1/2,-y+3/2,z+1/2; #4 -x+1/2,y-1/2,-z+1/2

Table S5 Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$.

The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2}$ U11 + ... + 2hka* b*U12].

Atom	U11	U22	U33	U12	U13	U23
Ca1	14.0(3)	13.8(4)	31.1(4)	0.2(2)	0	0
O1	28.7(11)	25.0(13)	44.9(14)	-9.7(8)	-0.1(10)	-4.6(11)
N3	13.3(9)	19.5(12)	41.3(15)	-0.7(9)	-0.6(9)	-1.8(12)
C4	17.4(11)	21.8(15)	27.4(16)	-0.3(10)	-0.1(11)	1.6(13)
C5	16.2(11)	17.7(14)	38.9(17)	1.0(10)	-3.2(12)	-4.5(14)
N6	21.8(10)	13.3(12)	37.9(14)	1.0(9)	0.9(11)	-2.0(11)
C7	18.8(11)	19.0(15)	25.2(14)	-4.4(9)	2.2(11)	-2.4(12)
C9	19.3(12)	16.9(14)	38.8(16)	0.7(10)	-2.8(13)	-2.4(13)
O0AA	14.9(8)	26.2(12)	47.2(15)	4.8(8)	-0.1(9)	3.5(11)
O2	22.4(9)	17.8(12)	80(2)	4.4(7)	2.2(10)	-10.6(12)
O1AA	158(6)	113(6)	33(3)	-98(5)	0	0

Table S6 Anisotropic displacement parameters (Å 2 ×10 3) for $Sr(H_5C_8N_4O_5)_2 \cdot 4H_2O$.

The anisotropic displacement factor exponent takes the form: -2π 2 [h 2 a* 2 U11 + ... + 2hka* b*U12].

Atom	U11	U22	U33	U12	U13	U23
Sr(1)	77(1)	27(1)	40(1)	-3(1)	14(1)	-4(1)
O(1)	42(6)	71(7)	35(5)	-5(5)	1(4)	-8(5)
O(2)	45(6)	66(7)	41(6)	-17(5)	-9(4)	23(5)
O(3)	57(6)	30(5)	31(5)	-11(3)	-7(4)	27(4)
O(4)	62(6)	91(8)	14(4)	-16(4)	13(4)	-56(6)
O(5)	97(4)	19(2)	45(3)	0(2)	12(3)	-10(2)
O(6)	85(4)	21(2)	46(3)	-5(2)	8(3)	-6(2)
O(7)	184(9)	33(3)	58(4)	-10(3)	32(5)	8(4)
O(8)	69(4)	43(3)	45(3)	-1(2)	15(3)	-8(3)
O(9)	104(5)	24(2)	47(3)	6(2)	23(3)	2(3)
O(10)	85(4)	25(2)	44(3)	-6(2)	13(3)	-4(2)
O(11)	76(4)	19(2)	45(3)	-4(2)	9(2)	2(2)
O(12)	74(4)	59(4)	40(3)	-4(3)	8(3)	5(3)
O(13)	79(4)	25(2)	38(3)	-3(2)	11(2)	3(2)
O(14)	83(4)	65(4)	38(3)	-5(3)	12(3)	4(3)
N(1)	58(4)	21(3)	45(3)	-4(2)	11(3)	-4(2)
N(2)	58(4)	24(3)	34(3)	0(2)	7(3)	-4(2)
N(3)	86(5)	30(3)	48(4)	6(3)	9(3)	5(3)

N(4)	77(4)	21(3)	44(3)	6(2)	10(3)	0(3)
N(5)	57(4)	27(3)	40(3)	4(2)	6(3)	-1(2)
N(6)	53(4)	24(3)	49(4)	2(2)	10(3)	2(2)
N(7)	77(4)	20(3)	40(3)	-2(2)	10(3)	-2(3)
N(8)	73(4)	23(3)	39(3)	-3(2)	17(3)	2(3)
C(1)	47(4)	30(3)	46(4)	-3(3)	4(3)	-5(3)
C(2)	47(4)	24(3)	42(4)	0(3)	1(3)	-3(3)
C(3)	35(3)	22(3)	49(4)	3(3)	5(3)	-3(2)
C(4)	37(3)	33(3)	40(4)	-2(3)	6(3)	-3(3)
C(5)	31(3)	24(3)	67(5)	9(3)	7(3)	1(2)
C(6)	43(4)	18(3)	53(4)	7(3)	8(3)	1(2)
C(7)	54(4)	33(3)	45(4)	2(3)	4(3)	2(3)
C(8)	98(7)	26(3)	41(4)	3(3)	14(4)	6(4)
C(9)	41(4)	26(3)	47(4)	-1(3)	9(3)	1(3)
C(10)	50(4)	25(3)	42(4)	1(3)	3(3)	-3(3)
C(11)	48(4)	25(3)	38(4)	1(3)	6(3)	5(3)
C(12)	35(3)	27(3)	47(4)	0(3)	7(3)	3(2)
C(13)	44(4)	20(3)	43(4)	-2(2)	4(3)	3(2)
C(14)	48(4)	23(3)	41(4)	2(3)	7(3)	-2(3)
C(15)	48(4)	22(3)	47(4)	-8(3)	9(3)	3(3)
C(16)	64(5)	25(3)	44(4)	-4(3)	14(3)	1(3)

Table S7. Geometrical Factors (g) at 1064 nm for $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$.

g_{311}/N	g_{322}/N	g_{333}/N
-0.061	0.084	-0.073

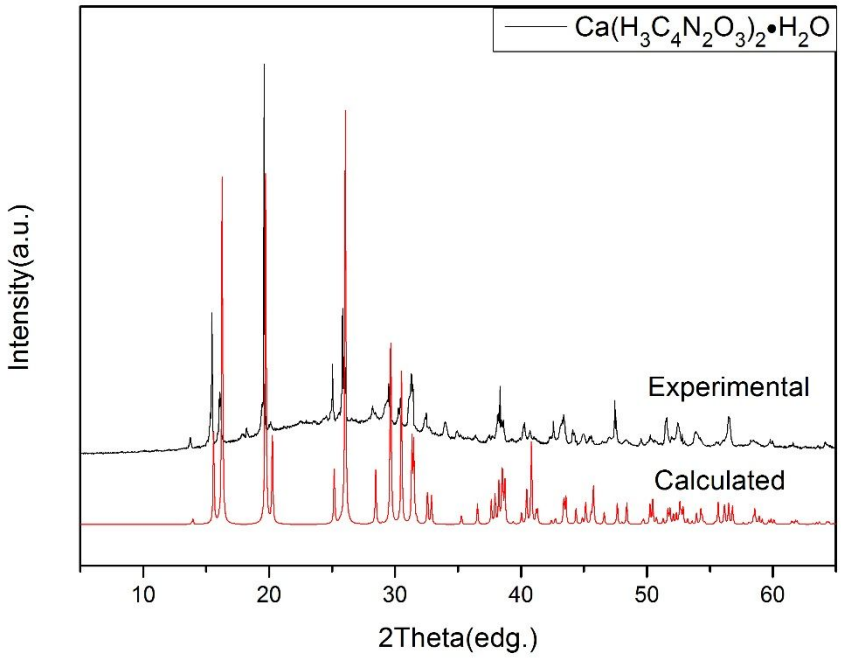

Figure S1. Experimental and calculated XRD patterns for $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$. The black curves are the patterns of samples, the red are the calculated ones.

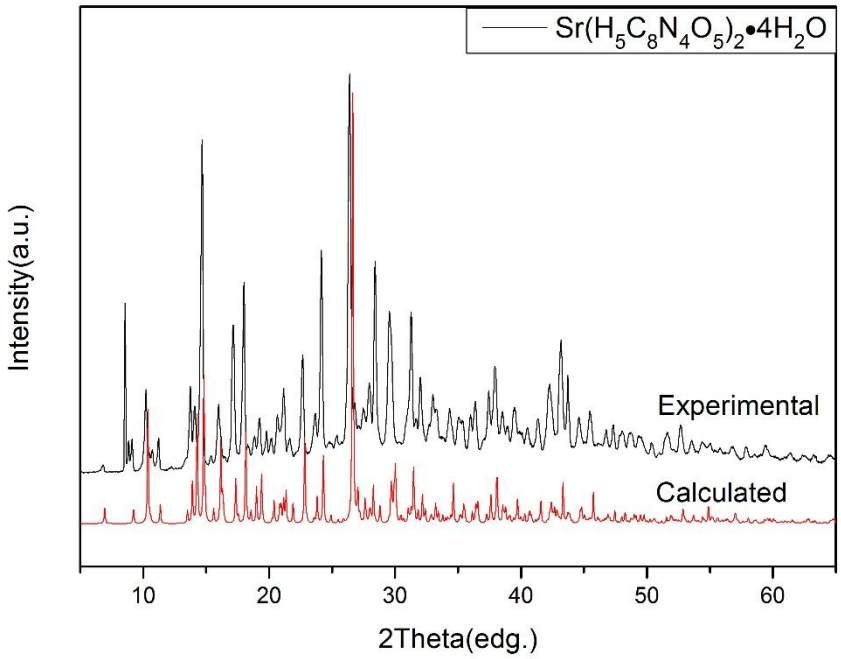

Figure S2. Experimental and calculated XRD patterns for $Sr(H_5C_8N_4O_5)_2 \cdot 4H_2O$. The black curves are the patterns of samples, the red are the calculated ones.

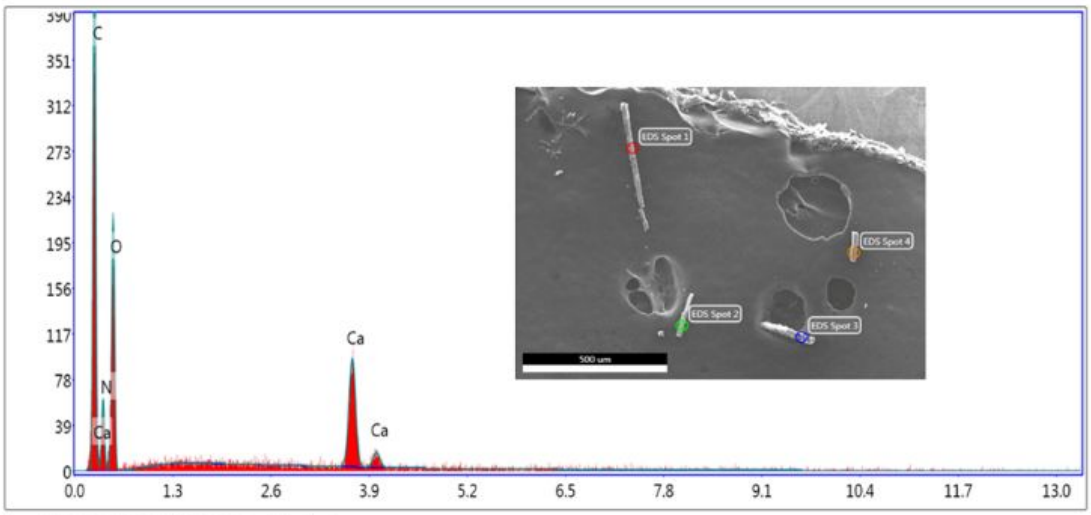

Figure S3. Energy dispersive X-ray spectroscopy analysis of $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$.

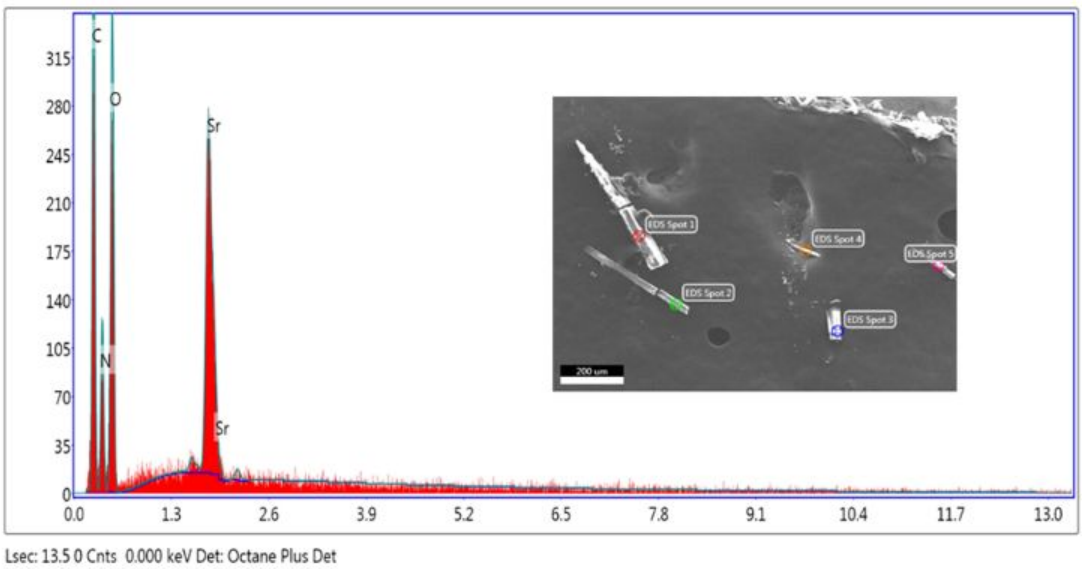

Figure S4. Energy dispersive X-ray spectroscopy analysis of $Sr(H_5C_8N_4O_5)_2 \cdot 4H_2O$.

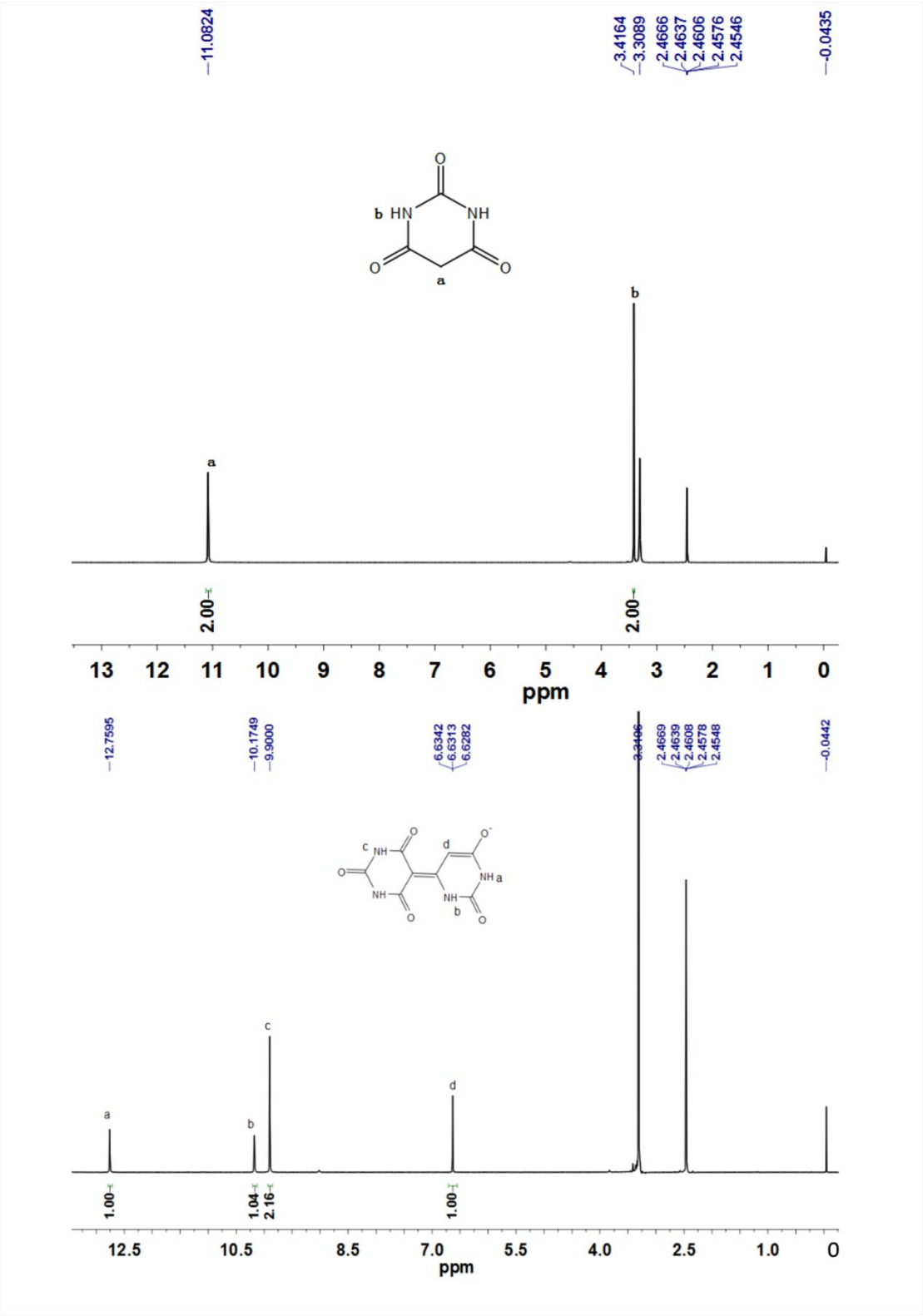

Figure S5. Nuclear magnetic resonance(NMR) spectroscopy of (a) ingredient ($H_4C_4N_2O_3$) and (b) crystal $Sr(H_5C_8N_4O_5)_2 \cdot 4H_2O$.

a:^{1}H NMR (DMSO-d_6, 600 MHz): δ /ppm = 11.08 (s, 2H), 3.42 (s,2H).

b:^{1}H NMR (DMSO-d_6, 600 MHz): δ /ppm = 12.76 (s, 1H), 10,17(s, 1H), 9.90(s,2H), 6.63(s,1H).

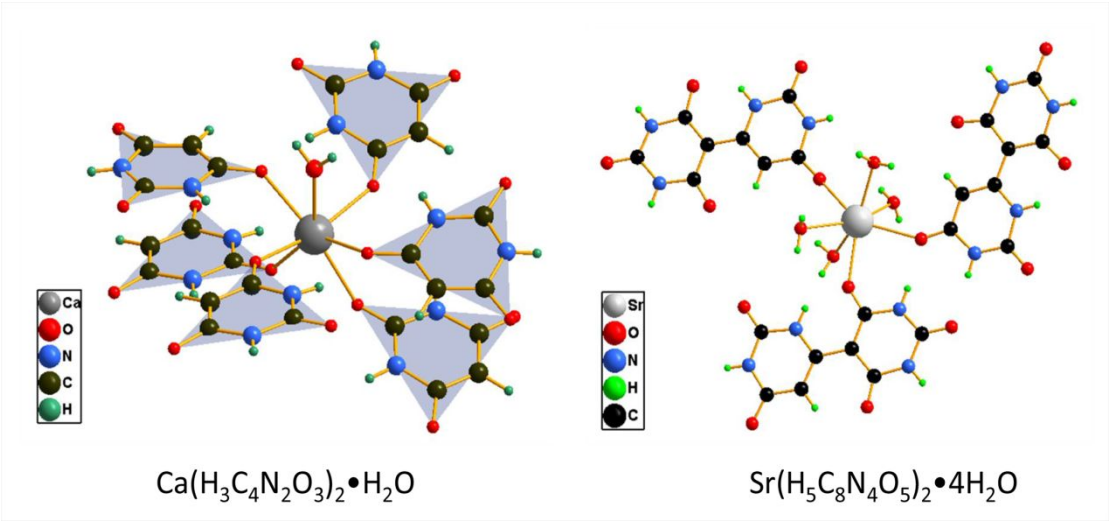

Figure S6. Coordination environment of metal cations in $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$ and $Sr(H_5C_8N_4O_5)_2 \cdot 4H_2O$.

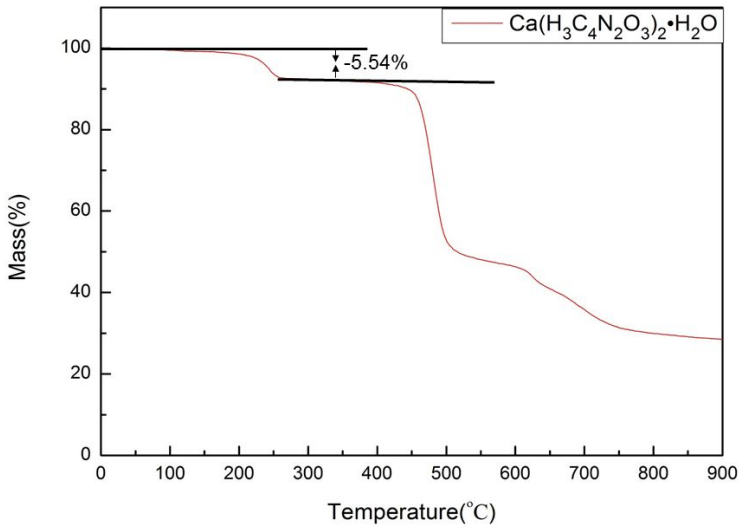

Figure S7. TG diagrams for $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$.

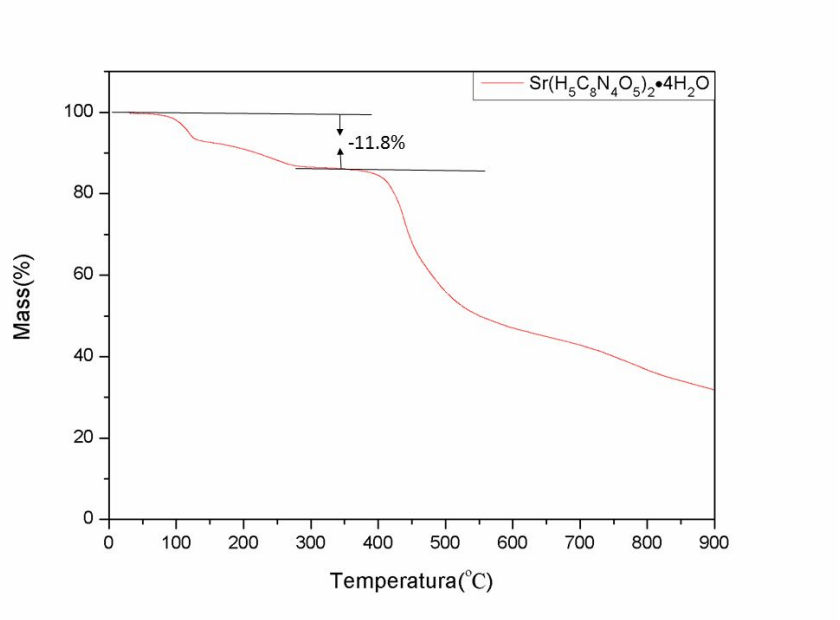

Figure S8. TG diagrams for $Sr(H_5C_8N_4O_5)_2 \cdot 4H_2O$.

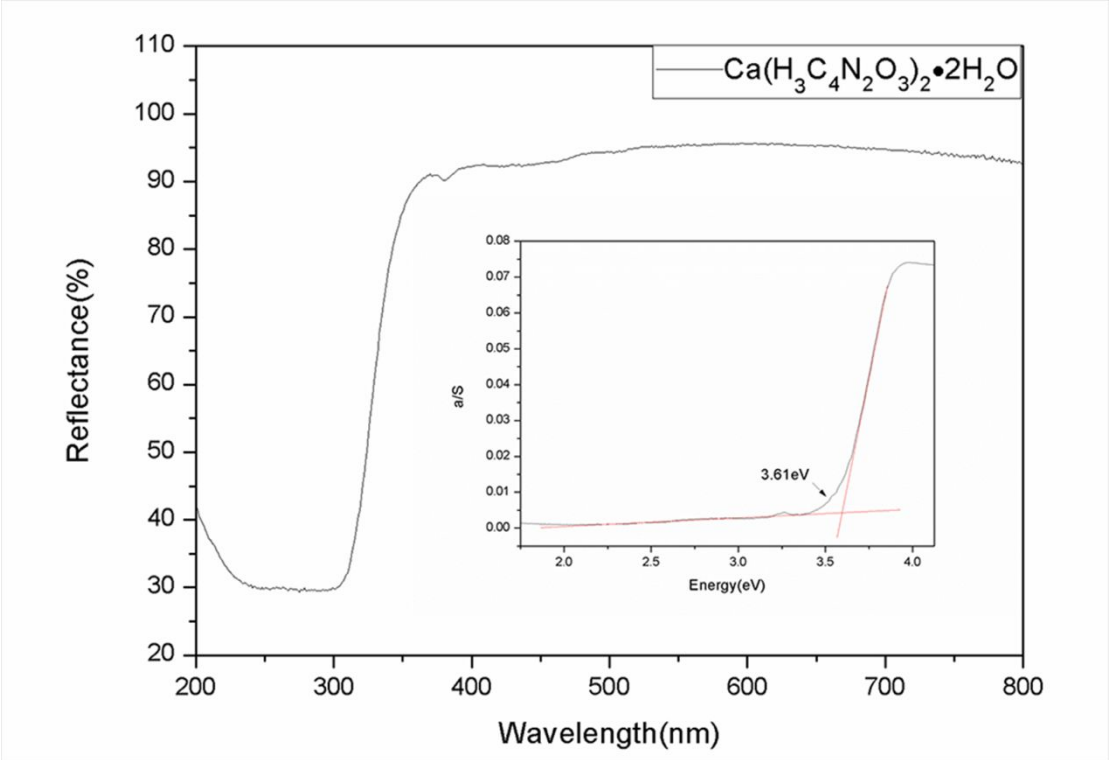

Figure S9. UV−vis−NIR diffuse reflectance spectrum of $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$.

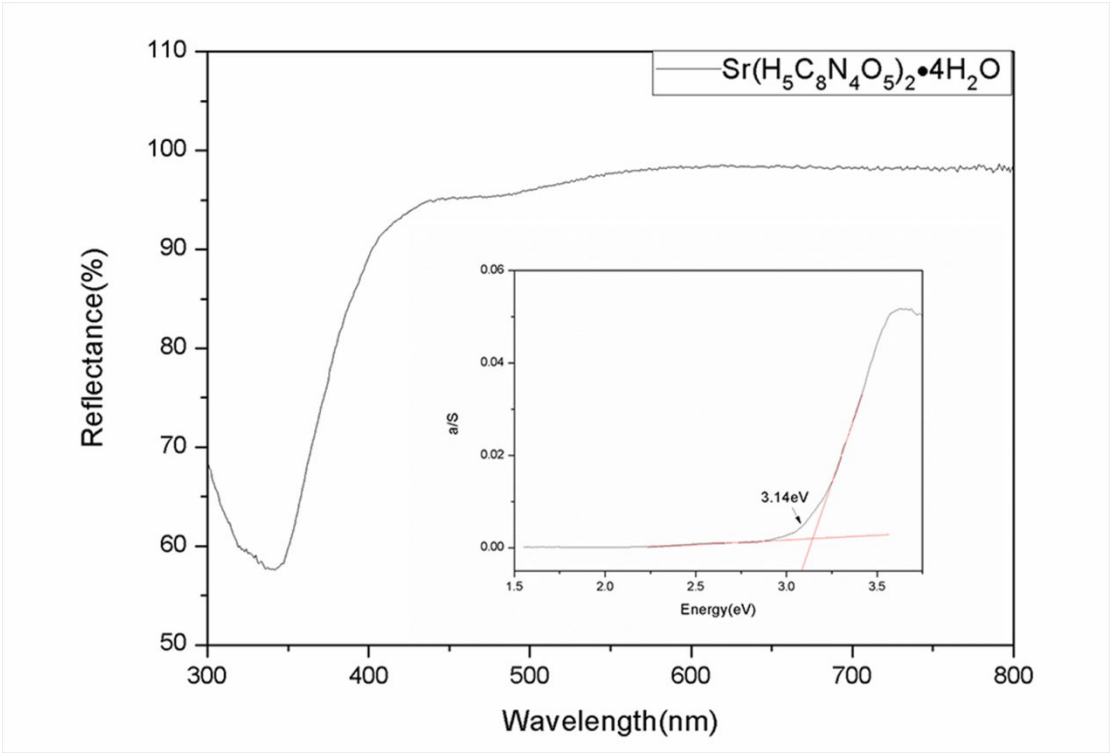

Figure S10. UV−vis−NIR diffuse reflectance spectrum of $Sr(H_5C_8N_4O_5)_2 \cdot 4H_2O$.

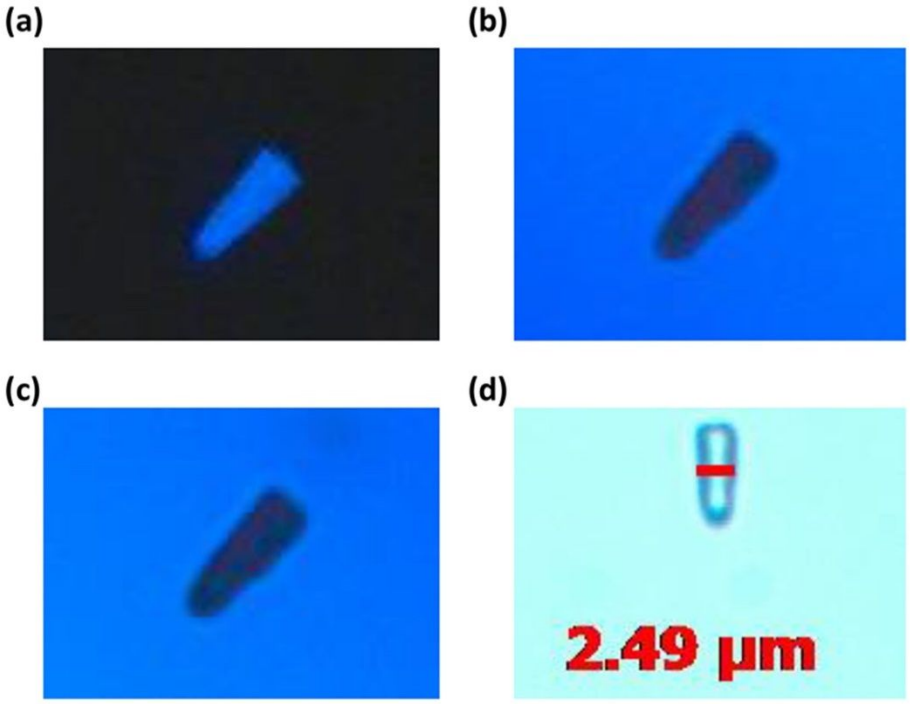

Figure S11. (a)Photograph of $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$ for the measurement of birefringence, and (b) the positive and (c) negative rotation of compensatory, and (d) the thickness of measured $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$ crystal.

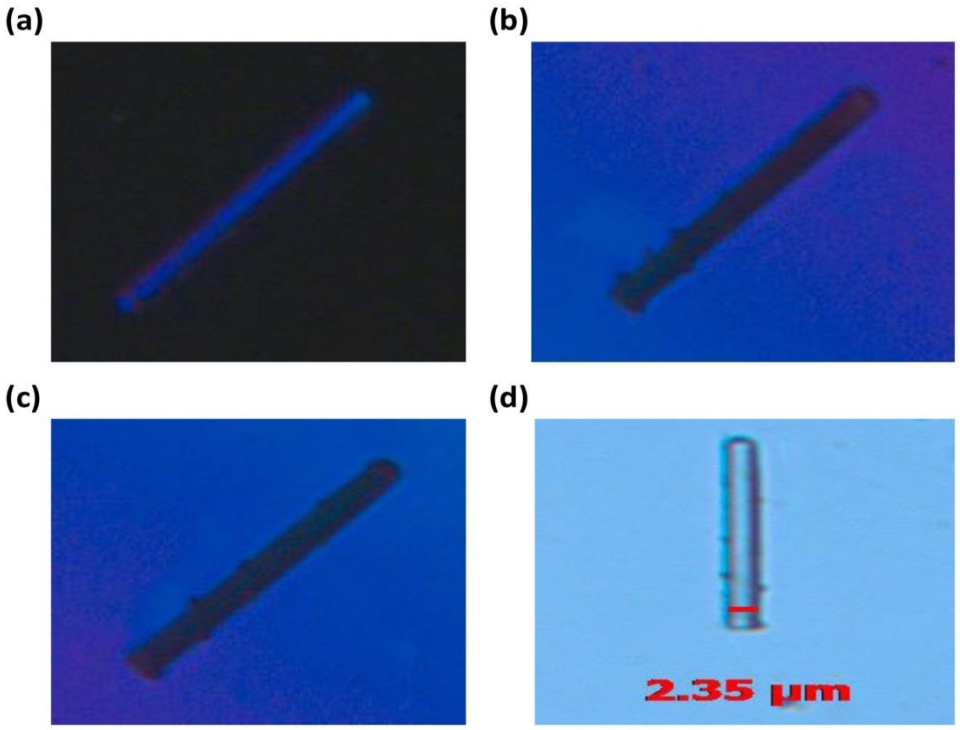

Figure S12. (a)Photograph of $Sr(H_5C_8N_4O_5)_2 \cdot 4H_2O$ for the measurement of birefringence, and (b) the positive and (c) negative rotation of compensatory, and (d) the thickness of measured $Sr(H_5C_8N_4O_5)_2 \cdot 4H_2O$ crystal.

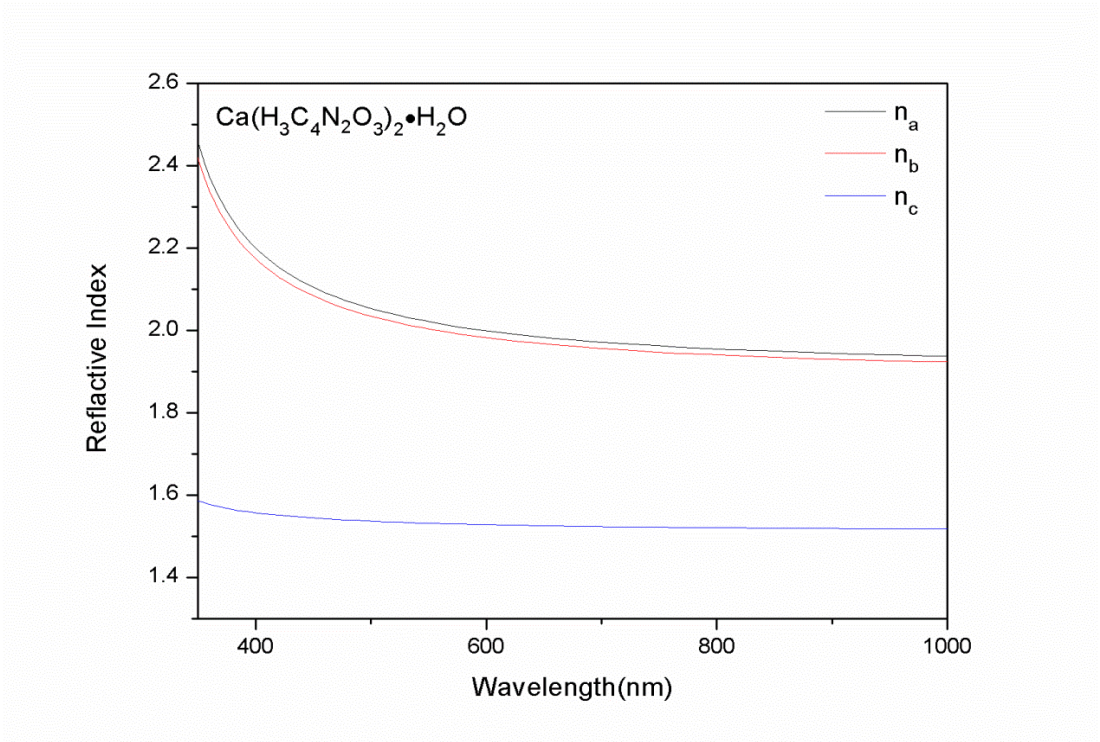

Figure S13. Calculated refractive indices of $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$.

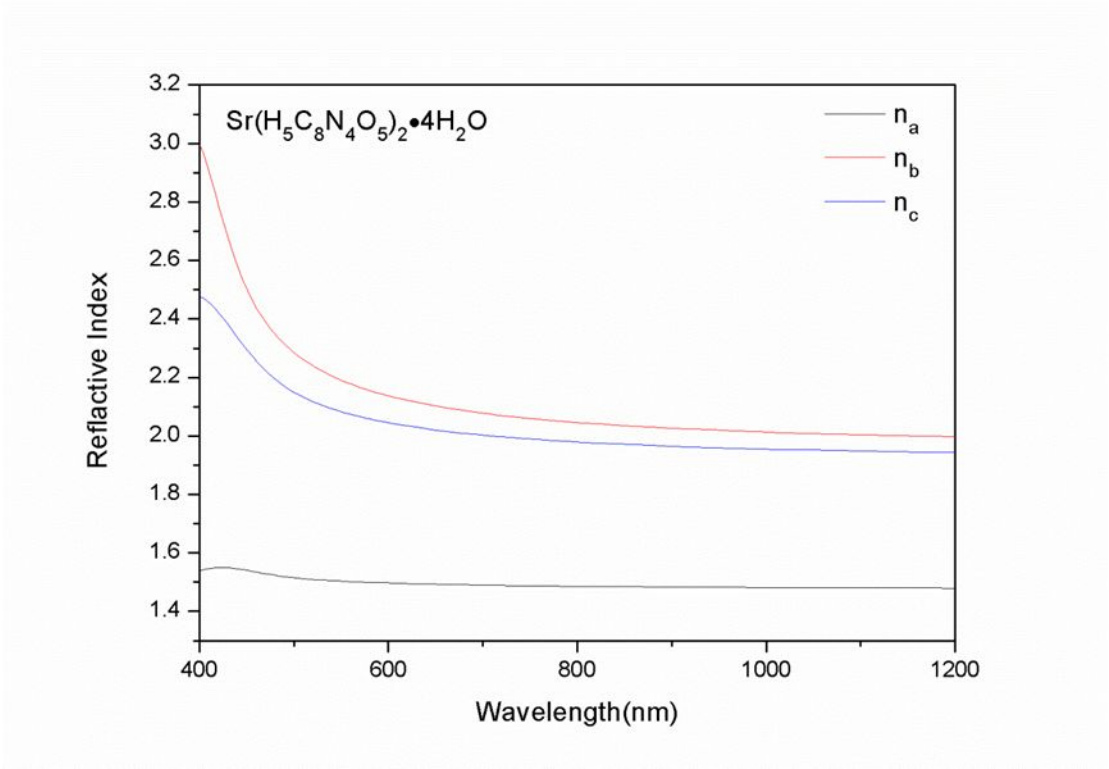

Figure S14. Calculated refractive indices of $Sr(H_5C_8N_4O_5)_2 \cdot 4H_2O$.

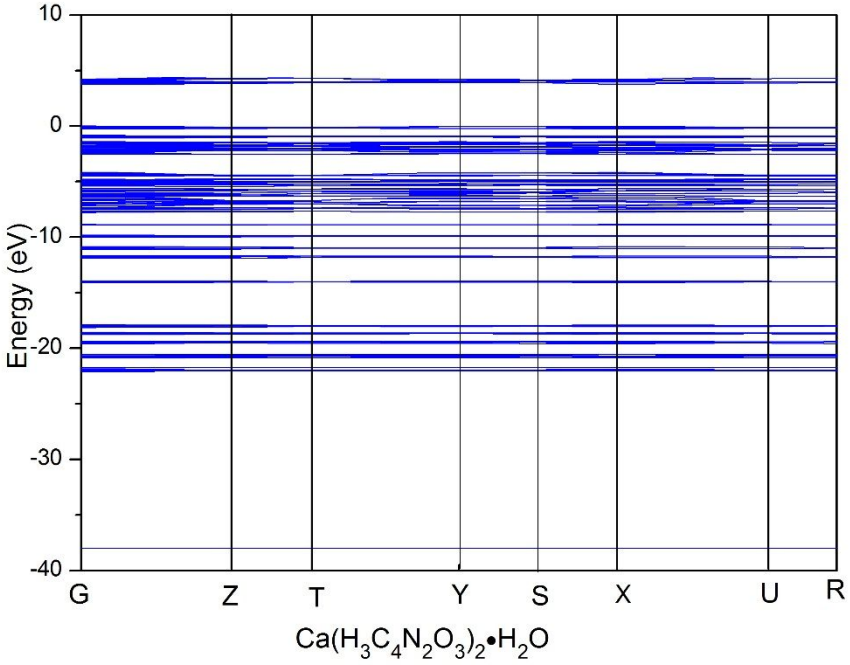

Figure S15. Band structures for $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$.

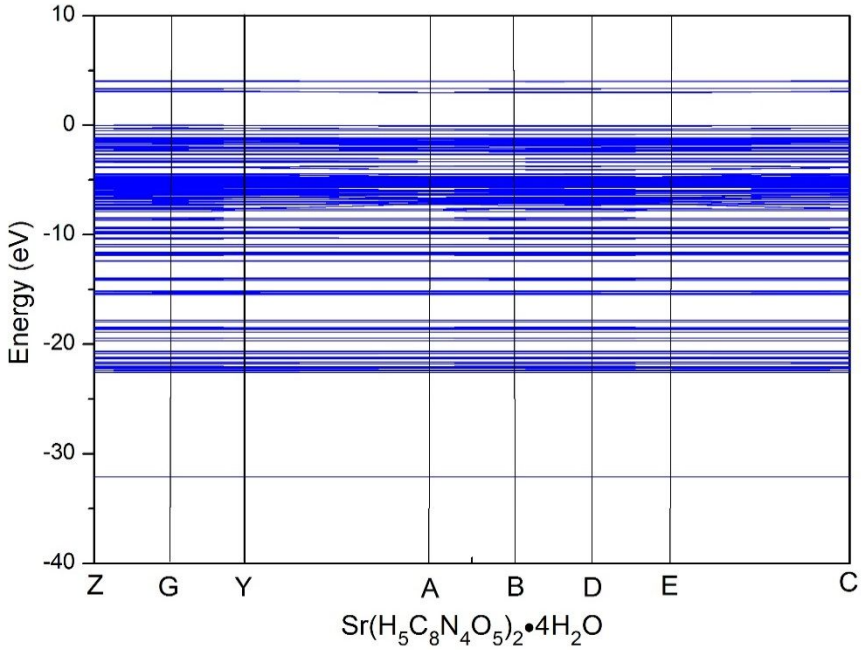

Figure S16. Band structures for $Sr(H_5C_8N_4O_5)_2 \cdot 4H_2O$.

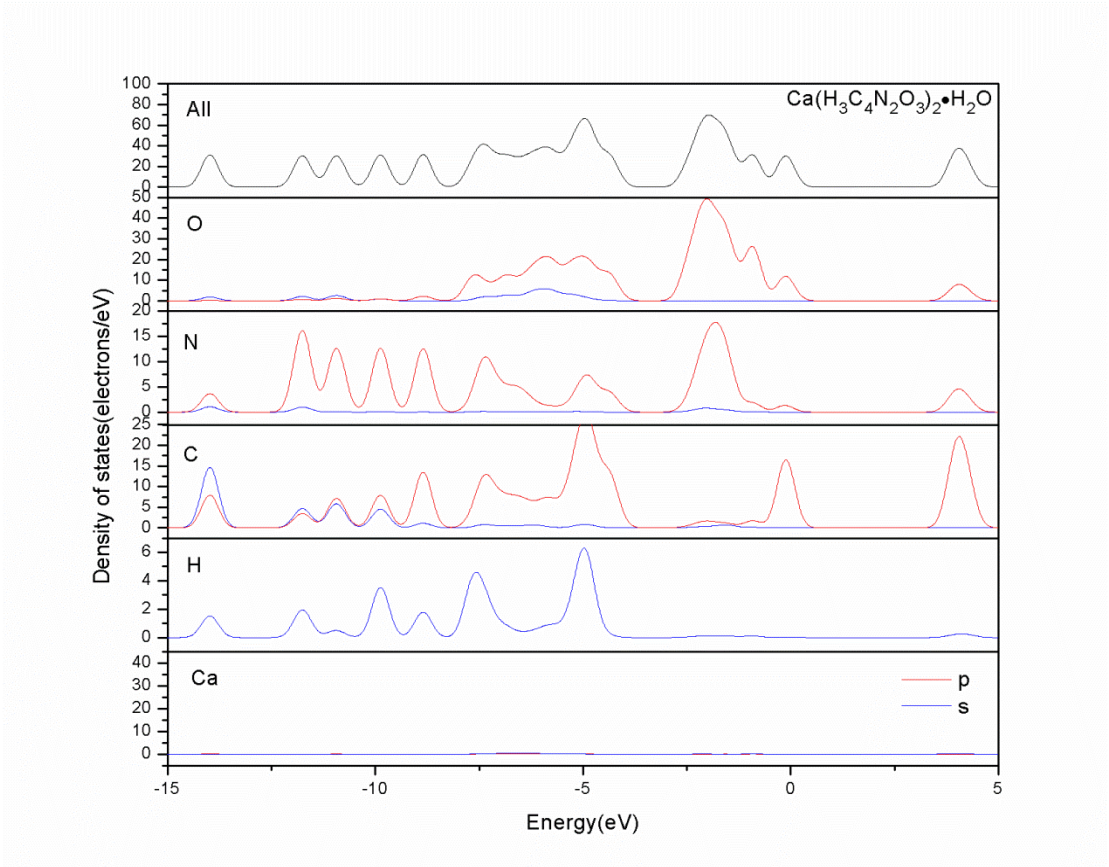

Figure S17. Densities of states for $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$.

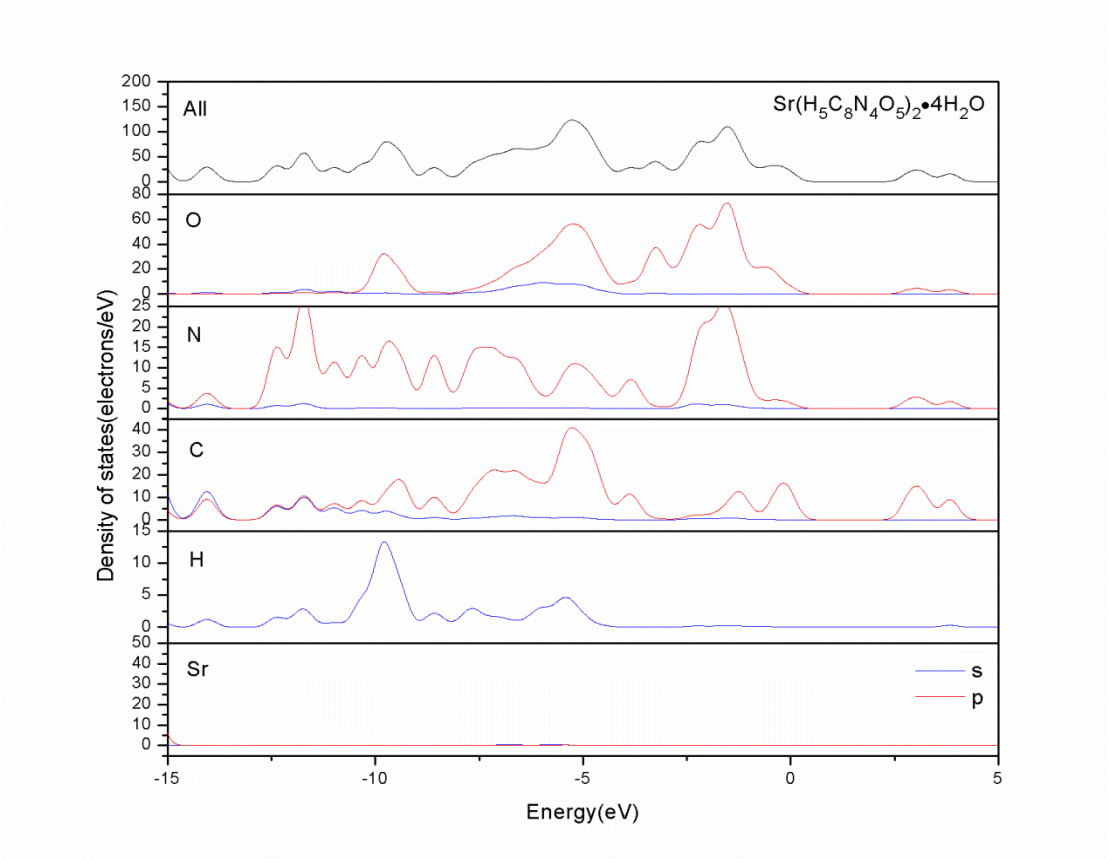

Figure S18. Densities of states for $Sr(H_5C_8N_4O_5)_2 \cdot 4H_2O$.

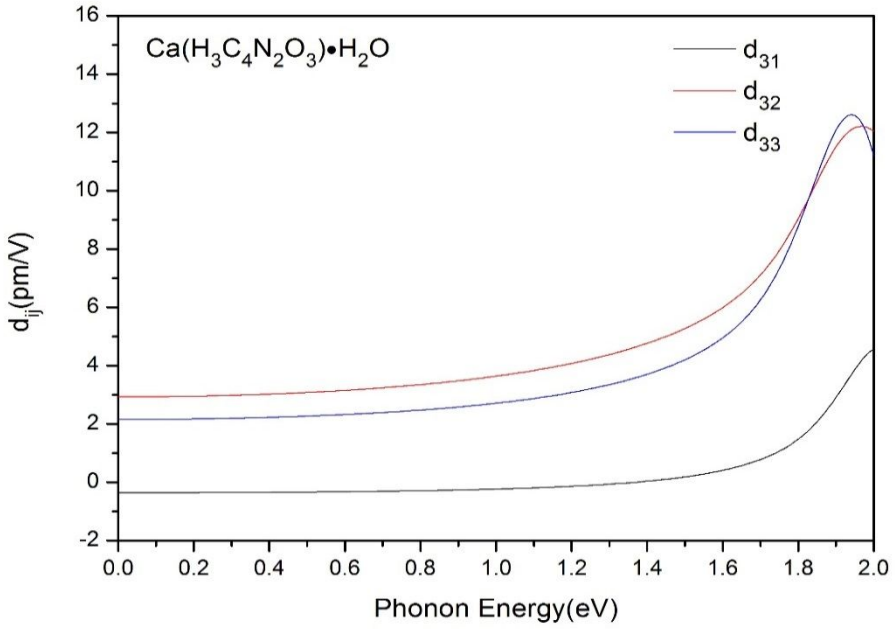

Figure S19. Calculated frequency-dependent second-harmonic generation coefficients for $Ca(H_3C_4N_2O_3)_2 \cdot H_2O$.

The Anionic Group Theory Calculation.

The macroscopic second-order susceptibility $\chi_{ijk}^{(2)}$ could be expressed by Eq. (1) according to the anionic group theory.

$$\chi_{ijk}^{(2)} = \frac{F}{V}\sum_{a,b,c} g_{ia,jb,kc} \cdot \beta_{abc}^{(2)} = \frac{F}{V} \cdot g_{ijk} \cdot \beta_{111}^{(2)} \quad (1)$$

$$\beta_{111}^{(2)} = -\beta_{122}^{(2)} = -\beta_{212}^{(2)} = -\beta_{221}^{(2)} \ (2)$$

where F is the correction factor of the localized field, V is the volume of the unit cell, α_{ia}, α_{jb}, and α_{kc} are the direction cosines between the macroscopic coordinate axes of the crystal and the microscopic coordinate axes of $(H_3C_4N_2O_3)^-$ groups, and β is the microscopic second-order susceptibility tensors of an individual group.

The geometrical factor g could be derived from Eq. (1).

$$g=\max(g_{ijk});\ (i,j,k=1,2,3)\ (3)$$

In case of unspontaneous polarization, the structural criterion C is defined as:

$$C = \frac{g}{n}\ (4)$$

where n is the number of anionic groups in a unit cell.