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Electronic Supplementary Information

$RbNa(HC_3N_3O_3)\cdot 2H_2O$ exhibiting strong second harmonic generation response and large birefringence as a new potential UV nonlinear optical material

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Table S1. Atomic coordinates and equivalent isotropic displacement parameters for $RbNa(HC_3N_3O_3)\cdot 2H_2O$.

atom	x	y	z	U(eq)
Rb(1)	1526(1)	5265(1)	5526(1)	34(1)
Na(1)	3206(2)	-11(5)	4000(2)	34(1)
C(1)	1404(4)	9290(19)	2997(6)	26(2)
C(2)	3390(3)	11928(16)	6388(5)	27(1)
C(3)	255(4)	9216(14)	1862(5)	26(1)
N(1)	567(3)	10042(10)	2799(4)	26(1)
N(2)	4225(3)	12675(13)	6168(4)	31(1)
N(3)	1919(3)	7817(12)	2308(4)	30(1)
O(1)	495(3)	10211(9)	6605(4)	34(1)
O(2)	2956(3)	10520(10)	5714(4)	37(1)
O(3)	1679(3)	10033(9)	3872(4)	34(1)
O(4)	4797(3)	267(8)	4146(4)	34(1)
O(5)	3342(4)	4894(10)	3109(6)	34(2)

Table S2. Bond lengths (Å) for $RbNa(HC_3N_3O_3)\cdot 2H_2O$.

Rb(1)-O(3)	2.881(5)	C(2)-N(2)	1.385(6)
Rb(1)-O(1)	2.914(5)	C(3)-O(1)#7	1.254(7)
Rb(1)-O(1)#1	2.943(4)	C(3)-N(1)	1.361(9)
Rb(1)-O(2)#1	2.954(5)	C(3)-N(2)#5	1.368(7)
Rb(1)-O(3)#1	3.005(5)	O(1)-C(3)#8	1.254(7)
Rb(1)-O(2)	3.086(5)	O(1)-Rb(1)#4	2.943(4)
Na(1)-O(5)	2.276(6)	O(2)-Na(1)#4	2.284(6)
Na(1)-O(2)#1	2.284(6)	O(2)-Rb(1)#4	2.954(5)
Na(1)-O(5)#1	2.341(6)	O(3)-Na(1)#4	2.424(7)
Na(1)-O(3)#1	2.424(7)	O(3)-Rb(1)#4	3.005(5)
Na(1)-O(4)	2.528(7)	N(2)-C(3)#6	1.368(7)
C(1)-O(3)	1.258(10)	N(3)-C(2)#5	1.345(6)
C(1)-N(3)	1.348(9)	O(5)-Na(1)#4	2.341(6)
C(1)-N(1)	1.382(9)	C(2)-N(3)#6	1.345(6)
C(2)-O(2)	1.249(7)		

Symmetry transformations used to generate equivalent atoms:

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

#4 x,y+1,z #5 -x+1/2,y-1/2,z-1/2

#6 -x+1/2,y+1/2,z+1/2 #7 -x,-y+2,z-1/2

#8 -x,-y+2,z+1/2 #9 -x+1/2,y+1/2,z-1/2 #10 x+1/2,-y+1/2,z

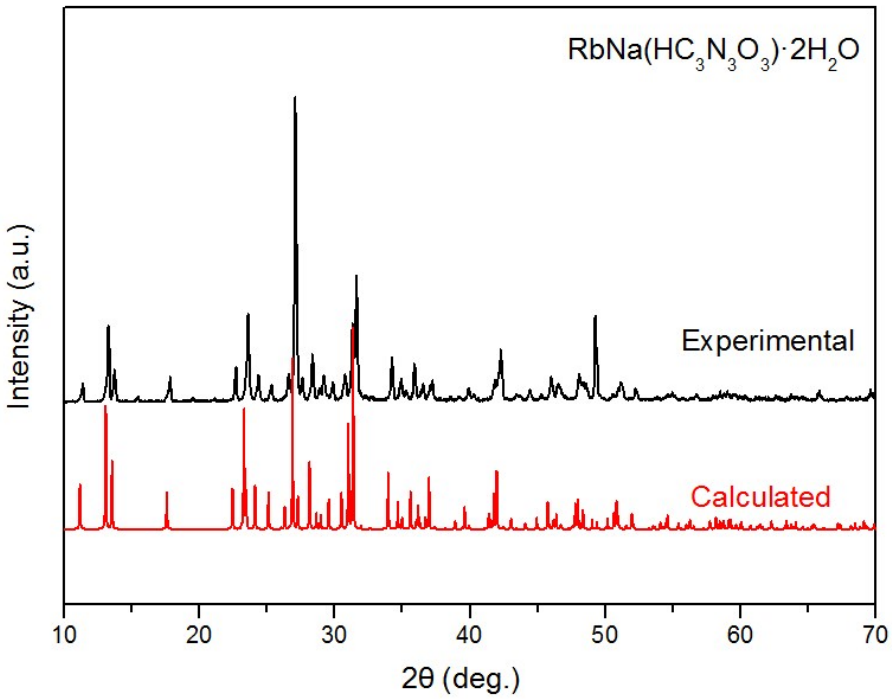

Fig. S1. Experimental and calculated XRD patterns for $RbNa(HC_3N_3O_3)\cdot 2H_2O$. The black curves are the patterns of samples, the red are the calculated ones.

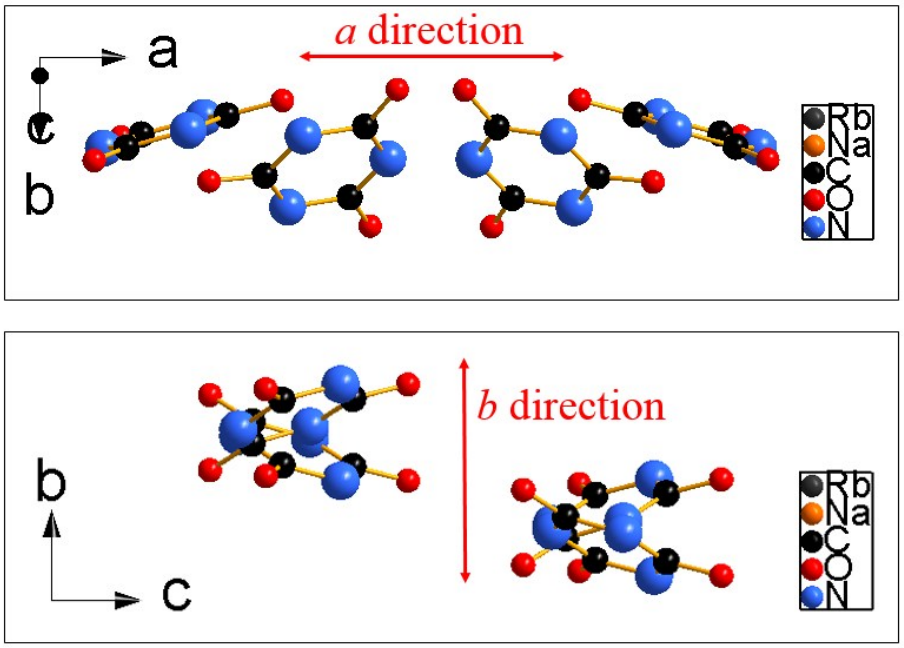

Fig. S2. Four kinds of $(HC_3N_3O_3)^{2-}$ groups exhibit opposite orientation in *a* axis and *b* axis due to the *n* slip plane and *a* slip plane for $RbNa(HC_3N_3O_3)\cdot 2H_2O$.

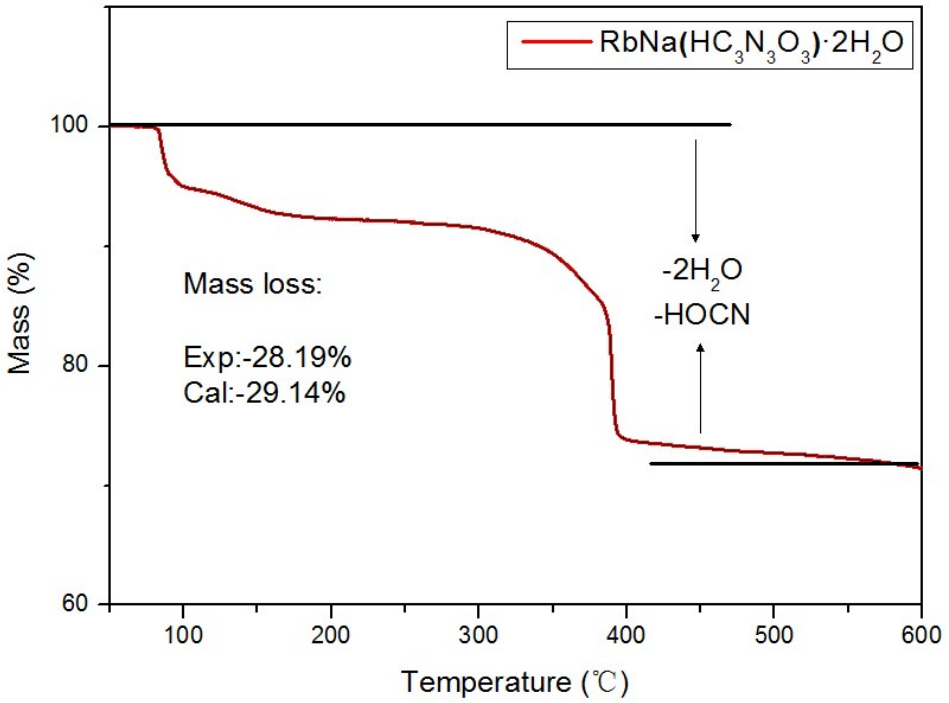

Fig. S3. TG diagrams for $RbNa(HC_3N_3O_3)\cdot 2H_2O$.

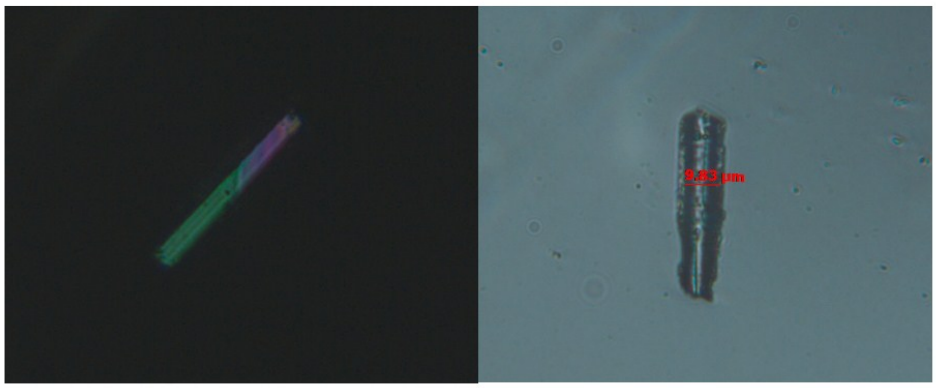

Fig. S4 (3) Photograph of crystal $RbNa(HC_3N_3O_3)\cdot 2H_2O$ for the measurement of birefringence.

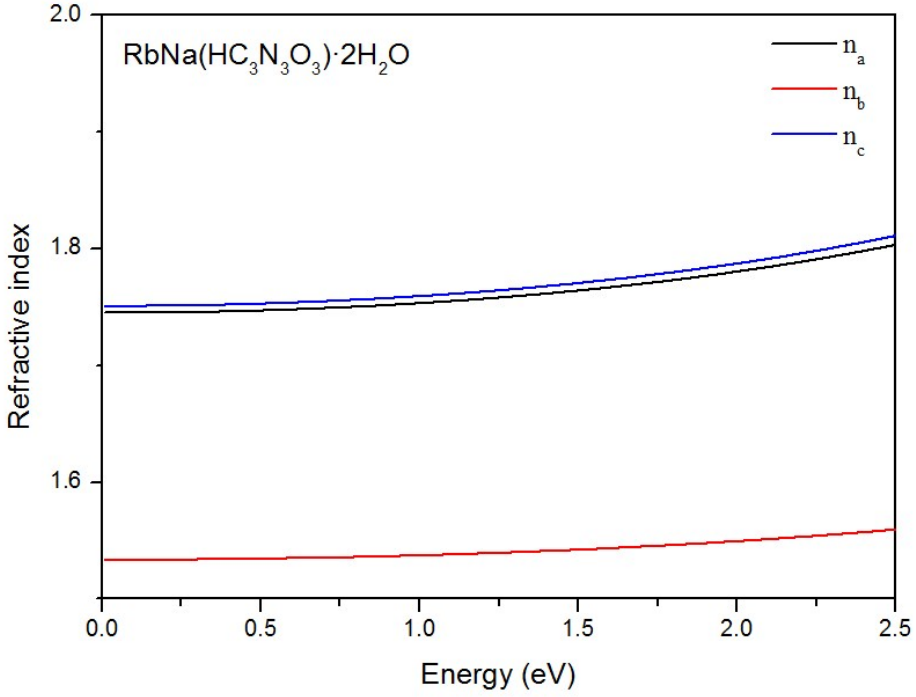

Fig. S5. Calculated refractive index for $RbNa(HC_3N_3O_3)\cdot 2H_2O$.

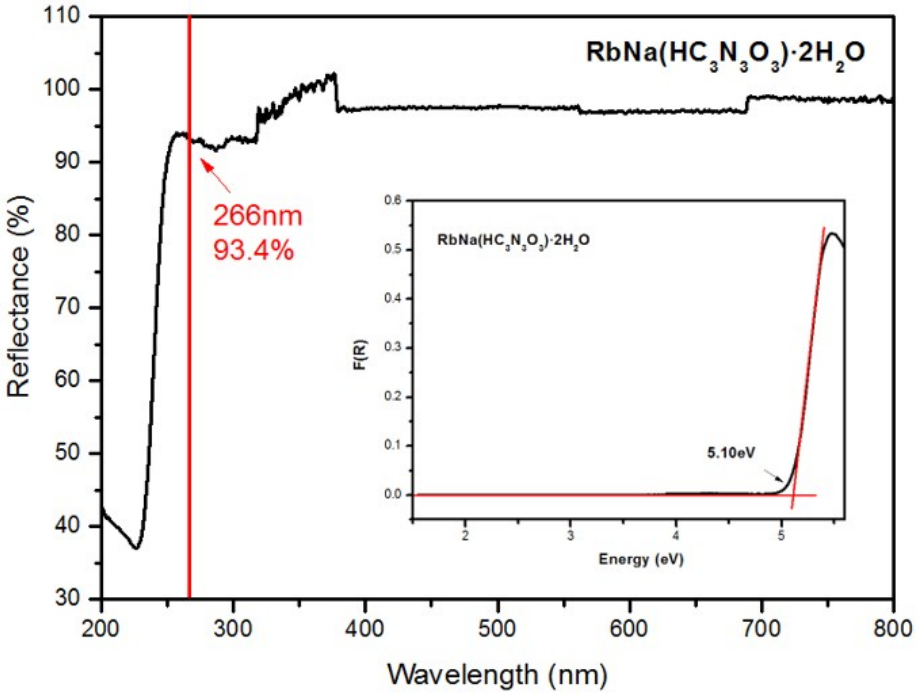

Fig. S6. Optical diffuse reflectance spectra for $RbNa(HC_3N_3O_3)\cdot 2H_2O$.

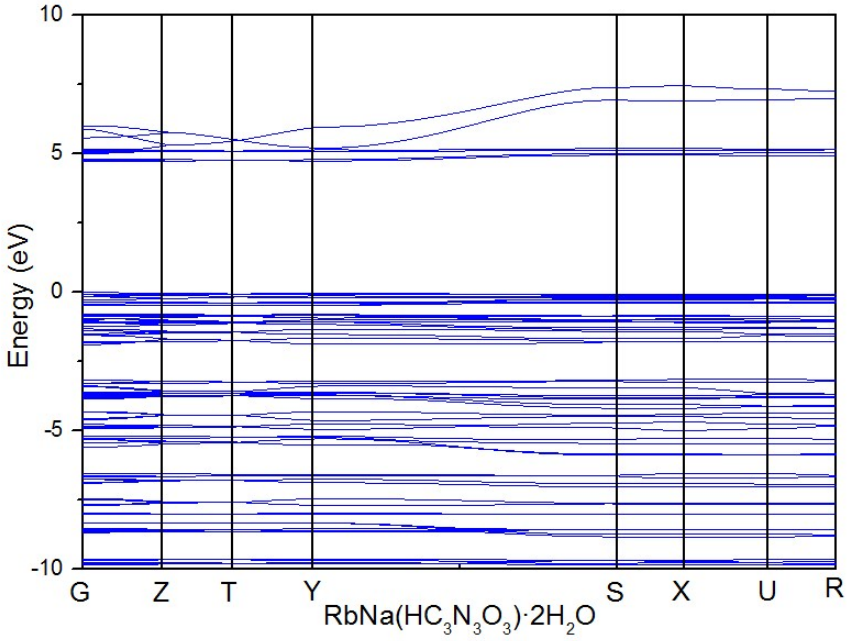

Fig. S7. Band structures for $RbNa(HC_3N_3O_3)\cdot 2H_2O$.

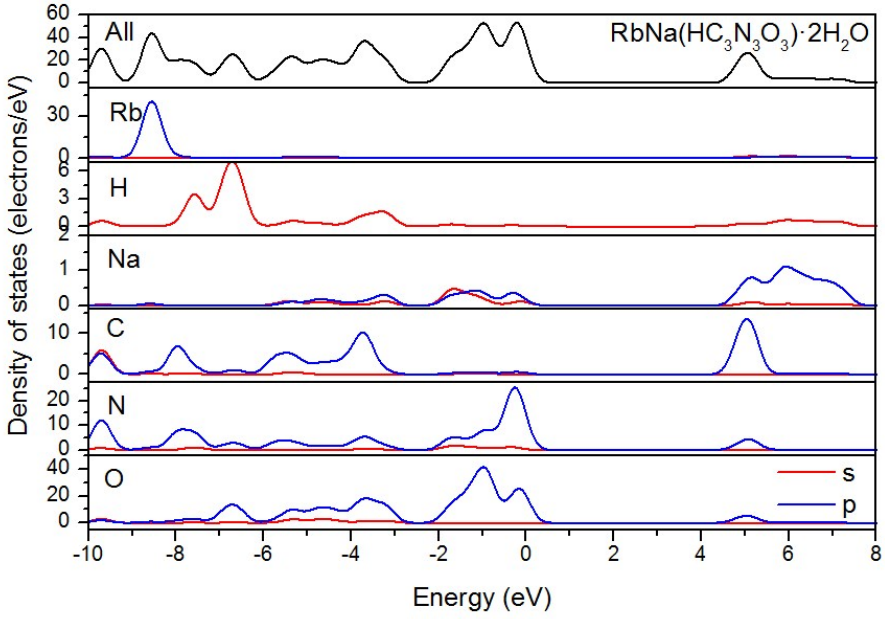

Fig. S8. Densities of states for $RbNa(HC_3N_3O_3)\cdot 2H_2O$.

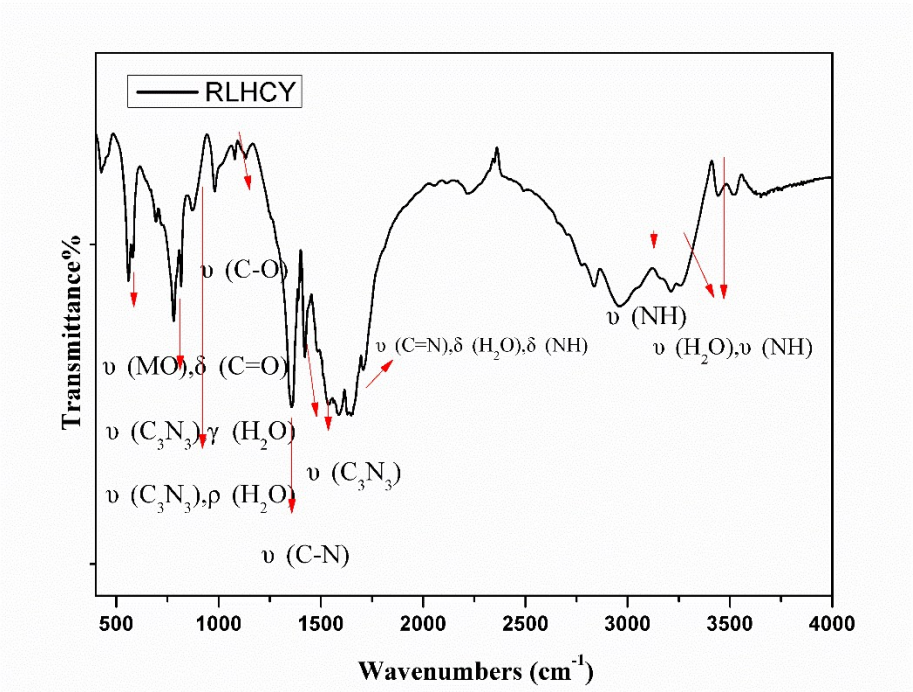

Fig. S9. The IR spectra of $RbNa(HC_3N_3O_3)\cdot 2H_2O$.

The Anionic Group Theory Calculation.

According to the anionic group theory, the dipole transition from the cations to the anionic group ($(HC_3N_3O_3)^{2-}$ in this case) is the off-site transition. Its value is about one order smaller than the dipole transition of the intra-atomic transitions within anionic groups. So the contribution to the main SHG coefficients from the anionic group $(HC_3N_3O_3)^{2-}$ is dominant, which is much larger than that of the charge transfer between the s-states of cations and the p-originated states of anions. Therefore, the macroscopic second-order susceptibility $\chi^{(2)}$ may be expressed by eq.1 on the basis of the anionic group theory,

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

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

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 $(HC_3N_3O_3)^{2-}$ groups, and β is the microscopic second-order susceptibility tensors of an individual group. Owing to the fact that $(HC_3N_3O_3)^{2-}$ is a planar group in point group D_{3h}, there are only two non-vanishing second-order susceptibility, under the Kleinman approximation. Because the geometrical factor g expressed by eq.3, eq.5 may be simplified according to the deduction process shown in the reference:

$$g_{ia,jb,kc} = \alpha_{ia}\alpha_{jb}\alpha_{kc} \quad (3)$$

$$\alpha_{i1} = \cos\theta_{i1} \quad (4)$$

$$g_{max} = max[mod(g_{ia,jb,kc})] \quad (5)$$

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

$$C = \frac{g_{max}}{n} \quad (6)$$

Where n is the number of anionic groups in a unit cell. Assuming an equal localized field (F) based on their similar refractive indices, we can deduce from the eq.5 and eq.6 that the NLO coefficient $\chi_{ijk}^{(2)}$ is proportional to density of the $(HC_3N_3O_3)^{2-}$ group (n/V) and the structural criterion(C).