Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.


# Electronic Supplementary Information (ESI)

# Optimized Arrangement of Non-π-Conjugated $PO_3NH_3$ Units Leads to Enhanced Ultraviolet Optical Nonlinearity in $NaPO_3NH_3$

Lingli Wu,[a, b, c] Haotian Tian,[b, c] Chensheng Lin,[b] Xin Zhao,[b, c] Huixin Fan,[b] Pengxiang Dong,[b] Shunda Yang,[b] Ning Ye,[d] and Min Luo*[a, b]

a Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, Fujian, 350108, China. E-mail: lm8901@fjirsm.ac.cn

b Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China.

c University of the Chinese Academy of Sciences, Beijing, 100049, China.

d Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystal, Tianjin University of Technology, Tianjin, 300384, China.

# Contents

**Table S1.** Crystal Data and Structure Refinement of $NaPO_3NH_3$.

| Formula | $NaPO_3NH_3$ |
|---|---|
| Formula weight | 79.33 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 1.54184 |
| Crystal system | Hexagonal |
| space group | P6(3) |
| a (Å) | 5.78050(10) |
| b (Å) | 5.78050(10) |
| c (Å) | 6.02650(10) |
| α (deg.) | 90 |
| β (deg.) | 90 |
| γ (deg.) | 120 |
| V ($Å^3$) | 174.392(7) |
| Z | 3 |
| Calculated density ($mg/m^3$) | 2.266 |
| Absorption coefficient ($mm^{-1}$) | 7.004 |
| F(000) | 120 |
| Theta range (deg.) | 8.859 to 76.177 |
| Limiting indices | -7<=h<=7 |
| | -7<=k<=7 |
| | -7<=l<=7 |
| Reflections collected / unique | 3022 / 253 |
| R(int) | 0.0256 |
| Completeness to θ = 67.684 (%) | 100.0 |
| Goodness-of-fit on $F^2$ | 1.166 |
| *R/wR* (I>2σ(I)) | R1 = 0.0244 |
| | wR2 = 0.0684 |
| *R/wR* (all data) | R1 = 0.0245 |
| | wR2 = 0.0684 |
| Absolute structure parameter | 0.07(8) |
| $^aR_1 = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$ | |
| $^b{}_wR_2(F_o^2) = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ | |

**Table S2.** Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $NaPO_3NH_3$.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| P(001) | 6667 | 3333 | 3811(3) | 13(1) |
| Na(02) | 10000 | 10000 | 5713(3) | 20(1) |
| O(003) | 7737(4) | 6233(4) | 3230(4) | 18(1) |
| N(004) | 6667 | 3333 | 6762(10) | 15(1) |

**Table S3**. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $NaPO_3NH_3$.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(00C) | 5295 | 3482 | 7254 | 18 |
| H(00B) | 8187 | 4705 | 7254 | 18 |
| H(00A) | 6518 | 1813 | 7254 | 18 |

**Table S4.** Selected Bond lengths (Å) and bond angles (°) for $NaPO_3NH_3$.

| | | | |
|---|---|---|---|
| P(001)-O(003)#1 | 1.510(2) | O(003)#4-Na(02)-O(003)#6 | 94.57(5) |
| P(001)-O(003)#2 | 1.509(2) | O(003)#5-Na(02)-O(003)#6 | 85.15(10) |
| P(001)-O(003) | 1.509(2) | O(003)#3-Na(02)-O(003)#7 | 94.57(5) |
| P(001)-N(004) | 1.779(6) | O(003)-Na(02)-O(003)#7 | 94.57(5) |
| Na(02)-O(003)#3 | 2.417(3) | O(003)#4-Na(02)-O(003)#7 | 179.62(11) |
| Na(02)-O(003) | 2.417(3) | O(003)#5-Na(02)-O(003)#7 | 85.15(10) |
| Na(02)-O(003)#4 | 2.417(3) | O(003)#6-Na(02)-O(003)#7 | 85.15(10) |
| Na(02)-O(003)#5 | 2.430(2) | O(003)#3-Na(02)-Na(02)#8 | 51.75(6) |
| Na(02)-O(003)#6 | 2.430(2) | O(003)-Na(02)-Na(02)#8 | 51.75(6) |
| Na(02)-O(003)#7 | 2.430(2) | O(003)#4-Na(02)-Na(02)#8 | 51.75(6) |
| Na(02)-Na(02)#8 | 3.01324(5) | O(003)#5-Na(02)-Na(02)#8 | 128.63(7) |
| Na(02)-Na(02)#6 | 3.01326(5) | O(003)#6-Na(02)-Na(02)#8 | 128.63(7) |
| N(004)-H(00C) | 0.8900 | O(003)#7-Na(02)-Na(02)#8 | 128.63(7) |
| N(004)-H(00B) | 0.8900 | O(003)#3-Na(02)-Na(02)#6 | 128.25(6) |
| N(004)-H(00A) | 0.8900 | O(003)-Na(02)-Na(02)#6 | 128.25(6) |
| O(003)#1-P(001)-O(003)#2 | 114.79(8) | O(003)#4-Na(02)-Na(02)#6 | 128.25(6) |
| O(003)#1-P(001)-O(003) | 114.79(8) | O(003)#5-Na(02)-Na(02)#6 | 51.37(7) |
| O(003)#2-P(001)-O(003) | 114.79(8) | O(003)#6-Na(02)-Na(02)#6 | 51.37(7) |
| O(003)#1-P(001)-N(004) | 103.41(11) | O(003)#7-Na(02)-Na(02)#6 | 51.37(7) |
| O(003)#2-P(001)-N(004) | 103.41(11) | Na(02)#8-Na(02)-Na(02)#6 | 180.0 |
| O(003)-P(001)-N(004) | 103.41(11) | P(001)-O(003)-Na(02) | 126.40(15) |
| O(003)#3-Na(02)-O(003) | 85.71(9) | P(001)-O(003)-Na(02)#8 | 151.40(15) |
| O(003)#3-Na(02)-O(003)#4 | 85.71(9) | Na(02)-O(003)-Na(02)#8 | 76.87(6) |
| O(003)-Na(02)-O(003)#4 | 85.71(9) | P(001)-N(004)-H(00C) | 109.5 |
| O(003)#3-Na(02)-O(003)#5 | 179.62(11) | P(001)-N(004)-H(00B) | 109.5 |
| O(003)-Na(02)-O(003)#5 | 94.57(5) | H(00C)-N(004)-H(00B) | 109.5 |
| O(003)#4-Na(02)-O(003)#5 | 94.57(5) | P(001)-N(004)-H(00A) | 109.5 |
| O(003)#3-Na(02)-O(003)#6 | 94.57(5) | H(00C)-N(004)-H(00A) | 109.5 |
| O(003)-Na(02)-O(003)#6 | 179.62(11) | H(00B)-N(004)-H(00A) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

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

#5 x-y+1,x,z+1/2  #6 -x+2,-y+2,z+1/2  #7 y,-x+y+1,z+1/2  #8 -x+2,-y+2,z-1/2

**Table S5.** Anisotropic displacement parameters ($Å^2 \times 10^3$) for $NaPO_3NH_3$.
The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| P(001) | 13(1) | 13(1) | 14(1) | 0 | 0 | 6(1) |
| Na(02) | 21(1) | 21(1) | 19(2) | 0 | 0 | 11(1) |
| O(003) | 18(1) | 15(1) | 20(1) | 2(1) | -1(1) | 8(1) |
| N(004) | 15(1) | 15(1) | 15(2) | 0 | 0 | 7(1) |

**Table S6.** Direction and magnitude of dipole moments of $[PO_3N]$ tetrahedron groups for NPNH and $[PO_3F]^{2-}$ in the unit cell.

| Compound | Species | Dipole moment (D) | | | |
|---|---|---|---|---|---|
| | | $\mu_x$ | $\mu_y$ | $\mu_z$ | $M_{total}$ |
| NPNH | $PO_3N$ | 0 | 0 | 5.01 | 5.01 |
| | $P'O_3N$ | 0 | 0 | 5.01 | 5.01 |
| | $\sum$ in unit cell | 0 | 0 | 10.02 | 10.02 |
| $NaNH_4PO_3F \cdot H_2O$ | $PO_3F$ | -0.03 | 1.45 | -6.37 | 6.53 |
| | $P'O_3F$ | -0.03 | -1.45 | -6.37 | 6.53 |
| | $P''O_3F$ | -0.02 | -1.45 | -6.37 | 6.53 |
| | $\sum$ in unit cell | -0.08 | -4.35 | -19.11 | 19.59 |

**Table S7.** The NLO properties of phosphates whose $\lambda_{cut\text{-}off}$ below 200 nm.

| FBUs | Crystal | Space group | SHG | Birefringence | Absorption edge (nm) | Ref. |
|---|---|---|---|---|---|---|
| $(PO_3)_\infty$ chain | $RbBa_2(PO_3)_5$ | *Pc* | 1.4 KDP | 0.009@1064 nm[b] | 163 | 1 |
| | $KBa_2(PO_3)_5$ | *Pc* | 0.9 KDP | n/a | 167 | 2 |
| | $KPb_2(PO_3)_5$ | *Pn* | 0.5 KDP | 0.030@589.3 nm[a] | 177 | 3 |
| | $KLa(PO_3)_4$ | $P2_1$ | 0.7 KDP | 0.0084@1064 nm[b] | 162 | 4 |
| | $CsLa(PO_3)_4$ | $P2_1$ | 0.5 KDP | 0.0068@1064 nm[b] | 167 | 5 |
| | $Cs_6Mg_6(PO_3)_{18}$ | $P2_1$ | 0.1 KDP | n/a | <190 | 6 |
| | $RbPb_2(PO_3)_5$ | *Pn* | 0.3 KDP | n/a | 163 | 3 |
| $[P_4O_{12}]^{4-}$ 8-M ring | $K_2SrP_4O_{12}$ | *I-4* | 0.5 KDP | 0.016@1064 nm[b] | <200 | 7 |
| $[P_3O_9]^{3-}$ 6-M ring | $BaNaP_3O_9$ | $P2_12_12_1$ | 0.3 KDP | n/a | 177 | 8 |
| $(P_2O_7)^{4-}$ dimer | $CsNaMgP_2O_7$ | $Cmc2_1$ | 1.1 KDP | n/a | 180 | 9 |
| | $RbNaMgP_2O_7$ (HTP) | $Ccm2_1$ | 1.4 KDP | 0.035@532nm[a] | 185 | 10 |
| | $RbNaMgP_2O_7$ (LTP) | $Pna2_1$ | 0.9 KDP | 0.031@532nm[a] | 185 | 10 |
| | $Ba_2NaClP_2O_7$ | *P4bm* | 0.9 KDP | 0.017@1064nm[b] | <176 | 11 |
| | $CsLiCdP_2O_7$ | $Pmc2_1$ | 1.5 KDP | n/a | <200 | 12 |
| | $Rb_2Ba_3(P_2O_7)_2$ | $P2_12_12_1$ | 0.3 KDP | n/a | <200 | 1 |
| | $Cs_2Ba_3(P_2O_7)_2$ | $P2_12_12_1$ | 0.4 KDP | n/a | <176 | 13 |
| | $K_4Mg_4(P_2O_7)_3$ | *Pc* | 1.3 KDP | 0.0108@1064nm[a] | 170 | 14 |
| | $Rb_4Mg_4(P_2O_7)_3$ | *Amm2* | 1.4KDP | 0.009@1064nm[b] | <200 | 14 |

| | | | | | | |
|---|---|---|---|---|---|---|
| $(P_3O_{10})^{5-}$ trimer | $Ba_3P_3O_{10}Cl$ | *Pca2₁* | 0.6KDP | 0.028@1064nm[b]<br>0.030@532nm[b] | 180 | 15 |
| | $Ba_3P_3O_{10}Br$ | *P2₁2₁2₁* | 0.5 KDP | 0.023@1064nm[b]<br>0.024@532nm[b] | <200 | 15 |
| | $Ba_5P_6O_{20}$ | *Pca2₁* | 0.8 KDP | n/a | 167 | 16 |
| Isolated $(PO_4)^{3-}$ | $LiCs_2PO_4$ | *Cmc2₁* | 2.6 KDP | 0.01@1064nm[b] | <174 | 17 |
| | $LiRb_2PO_4$ | *Cmc2₁* | 2.1 KDP | n/a | <170 | 18 |
| | $KMg(H_2O)PO_4$ | *Pmn2₁* | 1.14 KDP | 0.017@1064nm[b]<br>0.018@532nm[b] | <200 | 19 |
| | $BPO_4$ | *I-4* | 2 KDP | 0.00555@589nm[a] | 134 | 20 |
| $(PO_3F)^{2-}$ | $(NH_4)_2PO_3F$ | *Pna2₁* | 1 KDP | 0.030@589.3nm[a] | <185 | 21 |
| | $NaNH_4PO_3F{\cdot}H2O$ | *Pc* | 1.1 KDP | 0.053@589.3nm[a] | <200 | 22 |
| | $[C(NH_2)_3]_2PO_3F$ | *Cm* | 1.0 KDP | 0.039@532nm[b] | <200 | 23 |
| | $K_3Sc_3(PO_4)(PO_3F)_2F_5$ | *Cc* | 0.9 KDP | 0.026@546nm[a]<br>0.024@1064nm[a] | <200 | 24 |
| | $Cd(NH_4)_2(PO_3F)_2{\cdot}2H_2O$ | *Cmc2₁* | 0.78 KDP | 0.026@546nm[a] | <200 | 25 |
| | $K_x(NH_4)_{2-x}PO_3F(x=0\text{-}0.3)$ | *Pna2₁* | 1.0 KDP | 0.03@532nm[b] | <200 | 26 |
| | $Na_{1.5}Rb_{0.5}PO_3F{\cdot}H_2O$ | *Pmn2₁* | 0.55 KDP | 0.04@546nm[a] | <200 | 27 |
| $(PO_3NH_3)^-$ | $NaPO_3NH_3$ | *P6₃* | 0.80KDP | 0.062@546.1nm[b] | <190 | This work |

a for experiment, b for calculation, and n/a means not reported or not available.

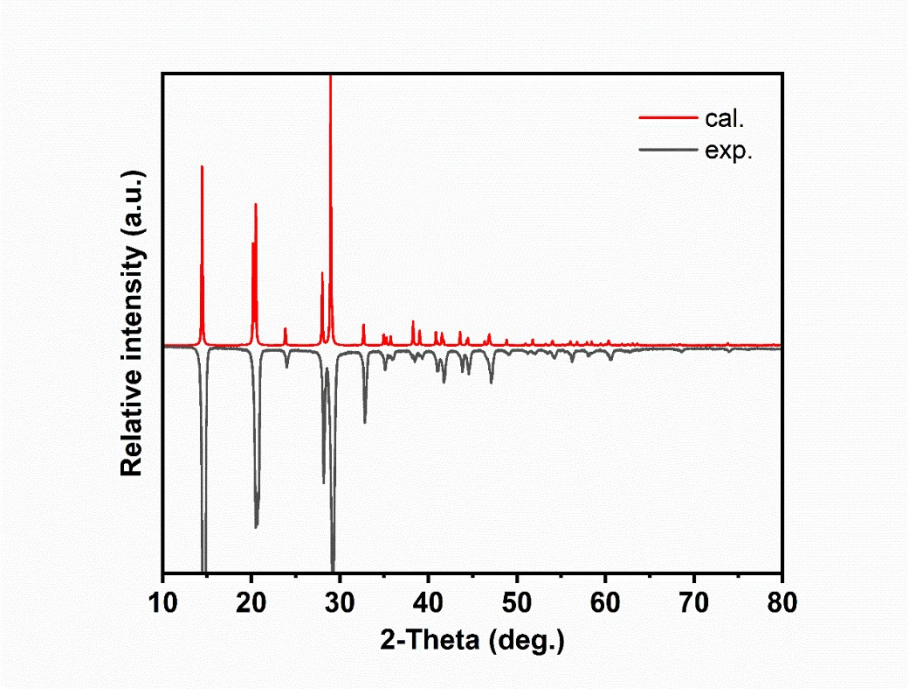


**Figure S1.** Calculated and experimental powder X-ray diffraction patterns of $NaPO_3NH_3$. No obvious impurity peaks were found, confirming the phase purity.

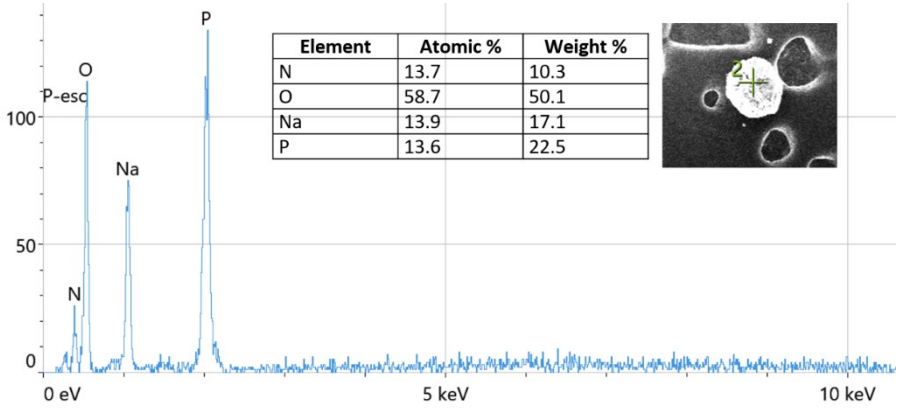


**Figure S2.** Energy dispersive X-ray spectroscopy analysis of $NaPO_3NH_3$.

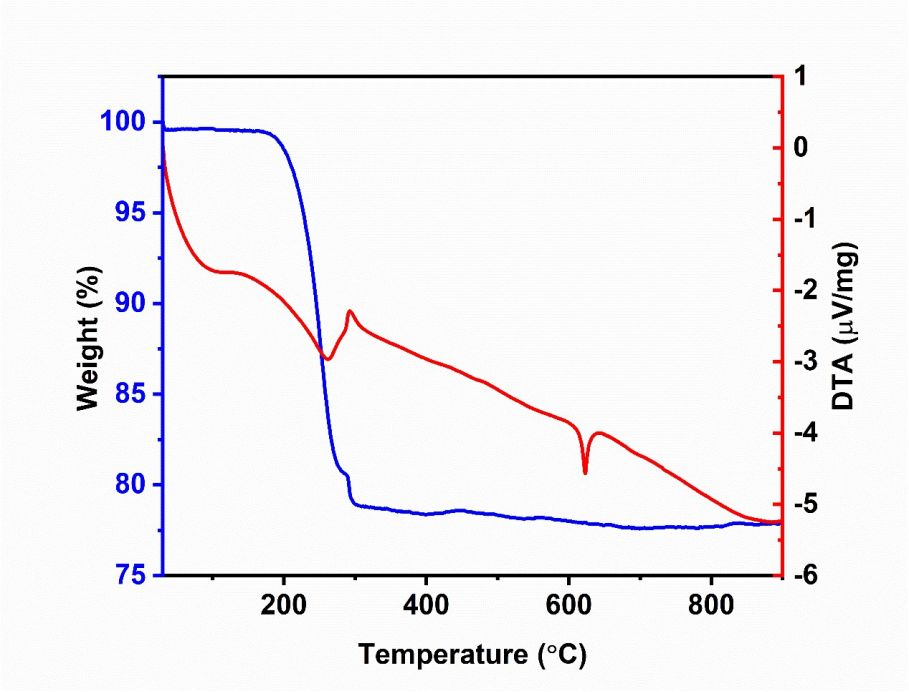


**Figure S3.** TG-DTA curves of $NaPO_3NH_3$.

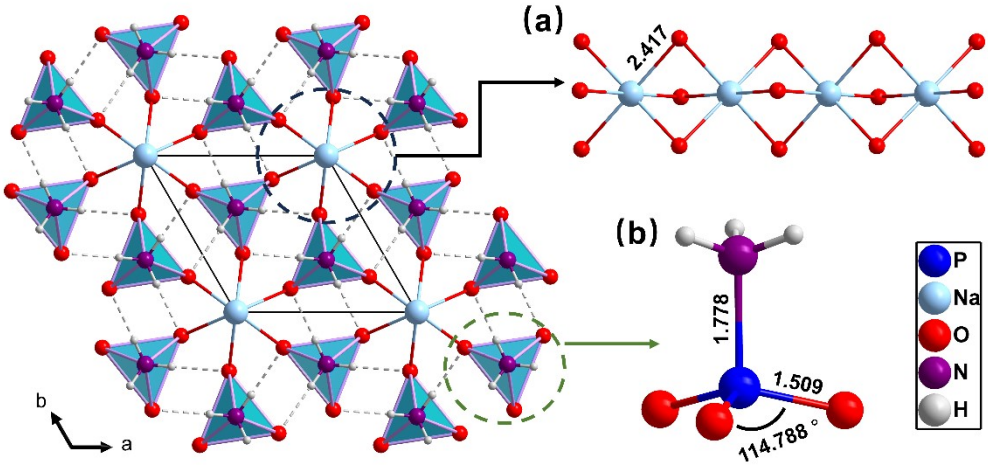


**Figure S4.** (a) Na-O chain; (b) $[PO_3NH_3]^-$ group. (The unit of interatomic distance is Å)

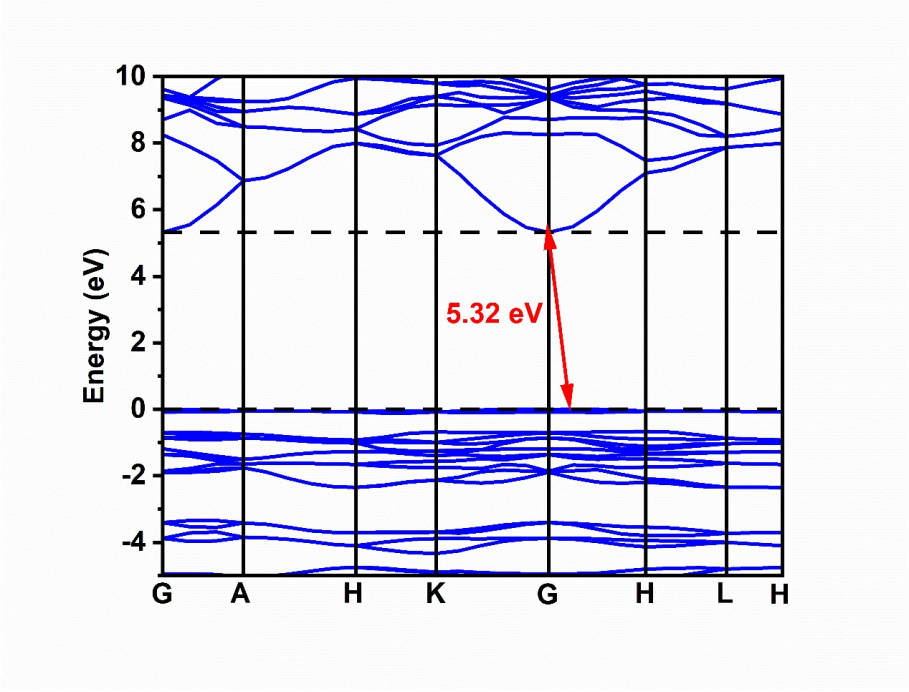


**Figure S5.** The calculated band structure of $NaPO_3NH_3$.

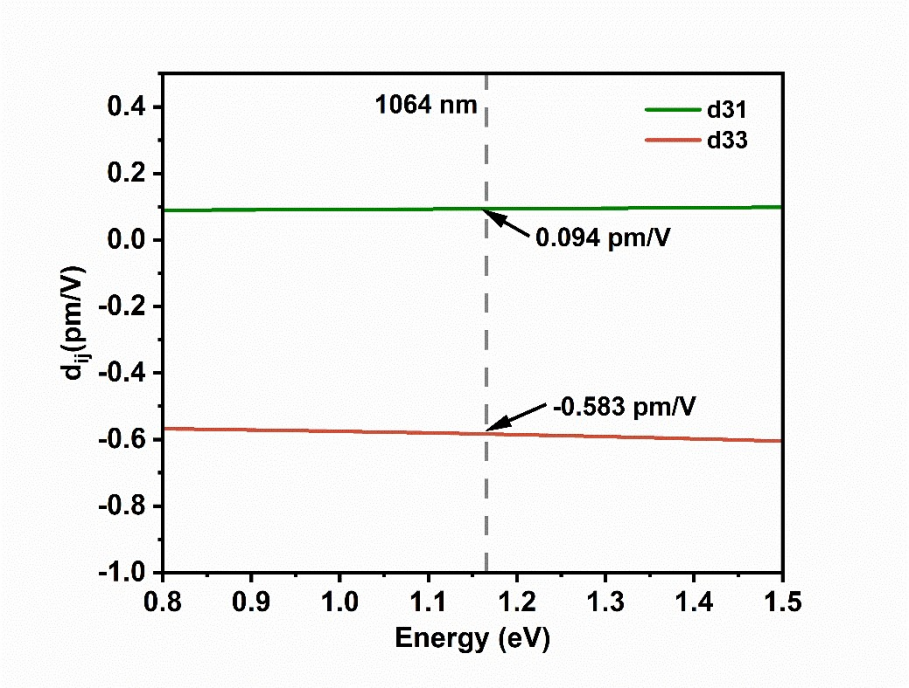


**Figure S6.** Calculated SHG coefficients of $NaPO_3NH_3$.

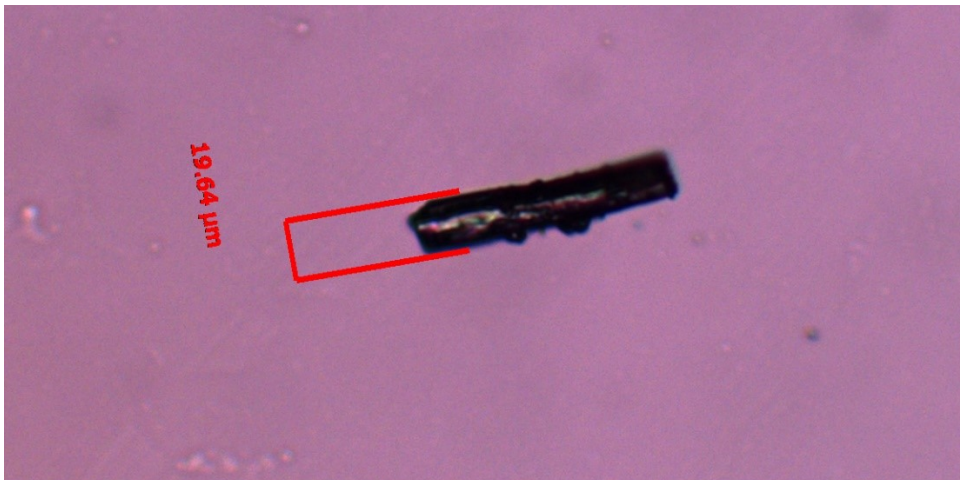


**Figure S7.** Single crystal of NPNH under the polarizing microscope. The measured thickness of NNPH is 19.64 μm.

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