

Electronic Supplementary Information

(N₂H₆)[HPO₃F]₂: Maximizing the Optical Anisotropy of Deep-Ultraviolet Fluorophosphates

Haotian Qiu,^{a,b} Fuming Li,^{a,b} Congcong Jin,^{a,b} Juanjuan Lu,^{a,b} Zhihua Yang,^{a,b} Shilie Pan^{a,b,*}
Miriding Mutailipu,^{a,b,*}

^aCAS Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics & Chemistry, CAS, and Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40-1 South Beijing Road, Urumqi 830011, China

^bCenter of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

*To whom correspondence should be addressed: E-mails: miriding@ms.xjb.ac.cn and slpan@ms.xjb.ac.cn.

Experimental Section

Crystal Growth. Single crystals of $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$ were grown *via* mild hydrothermal reaction without water. A mixture of $\text{N}_2\text{H}_6\text{F}_2$ (0.865g) and P_2O_5 (1.135g) with the molar ratio of 1.5:1 was put into a 25 mL Teflon-lined autoclave. They are heated to 110 °C for 80 h, and then slowly cooled to 70 °C at a rate of 0.01 °C/min; then quickly cooled to room temperature. With this process, the colorless $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$ crystals were obtained. To remove the impurities (a small amount of unknown phases with), crystals were washed quickly with water and alcohol, then placed on filter paper to dry. In addition, $\text{N}_2\text{H}_6\text{F}_2$ was synthesized by mixing $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (50 %) and excess HF (analytical purity). Single-crystal X-ray diffraction analysis was used to determine the crystal structure and powder X-ray diffraction measurement was applied to confirm the purity of as-prepared polycrystalline samples (see Figure S1).

Single Crystal Structure Data Collection. The single crystal diffraction data were collected on a Bruker D8 Venture Single Crystal X-ray Diffractometer (Mo $\text{K}\alpha$ radiation with $\lambda = 0.71073 \text{ \AA}$) at 300 K. Data integration, cell refinement and absorption corrections of the data were completed by utilizing SAINT program.¹ The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using the program suite SHELXL.² No missed symmetry was proved using PLATON program.³

Powder X-ray Diffraction Powder X-ray diffraction measurements for the targeted $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$ were carried out on a Bruker D2 PHASER diffractometer equipped with Cu $\text{K}\alpha$ radiation at room temperature. The 2θ range is 10-65 ° with a step size of 0.02 ° and a fixed counting time of 1 s/step.

Characterizations. TG and DSC analyses were carried out on a simultaneous NETZSCH STA 449 F3 thermal analyzer instrument in a flowing N_2 atmosphere. The powder sample of $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$ was placed in the Pt crucible, heated from 40 to 500 °C at a rate of 5 °C min^{-1} . The infrared spectroscopy was measured on a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in the 400-4000 cm^{-1} range. The

UV-vis-NIR diffuse-reflectance spectroscopy data were recorded at 25 °C using a powder sample of $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$ on a Shimadzu SolidSpec-3700DUV spectrophotometer. The polycrystalline powder of $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$ was prepared for the measurement of solid-state NMR. A Bruker Advance III 500 WB (11.75 T) spectrometer was utilized. The instrument was equipped with a DVT quadruple resonance H/F/X/Y 2.5 mm CP/MAS probe (spinning frequency = 30 kHz). PTFE, abundant with CF_2 groups, was used as the external reference of ^{19}F chemical shifts. The existence of P-F bonds was checked employing ^{31}P and ^{19}F NMR spectroscopy.

Computational Methods. The first-principles calculations were performed by the plane-wave pseudopotential method implemented in the CASTEP package.⁴ To achieve energy convergence, the kinetic energy cutoff of 850 eV for $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$ within normal-conserving pseudopotential (NCP) was adopted.⁵ The Monkhorst-Pack k-point meshes in the Brillouin zone was set as $4 \times 4 \times 3$ for $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$.

Figure S1. The experimental and calculated PXRD patterns of $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$.

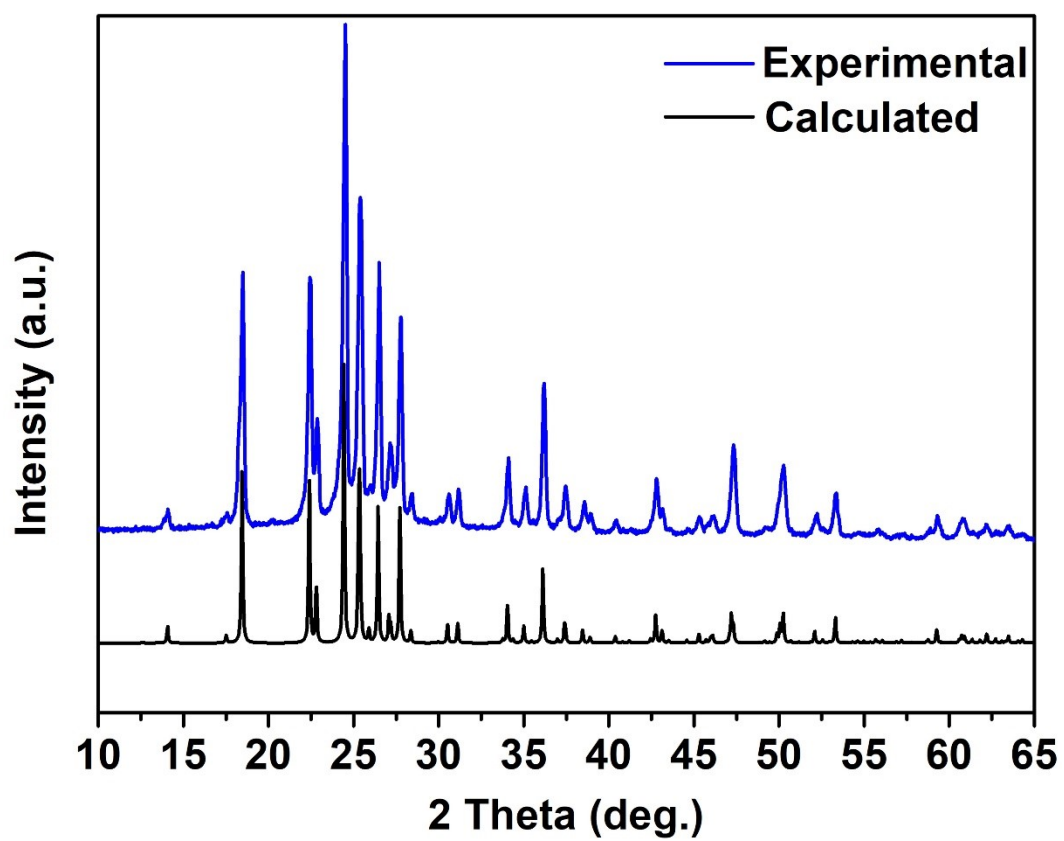


Figure S2. The TG and DSC curves of $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$.

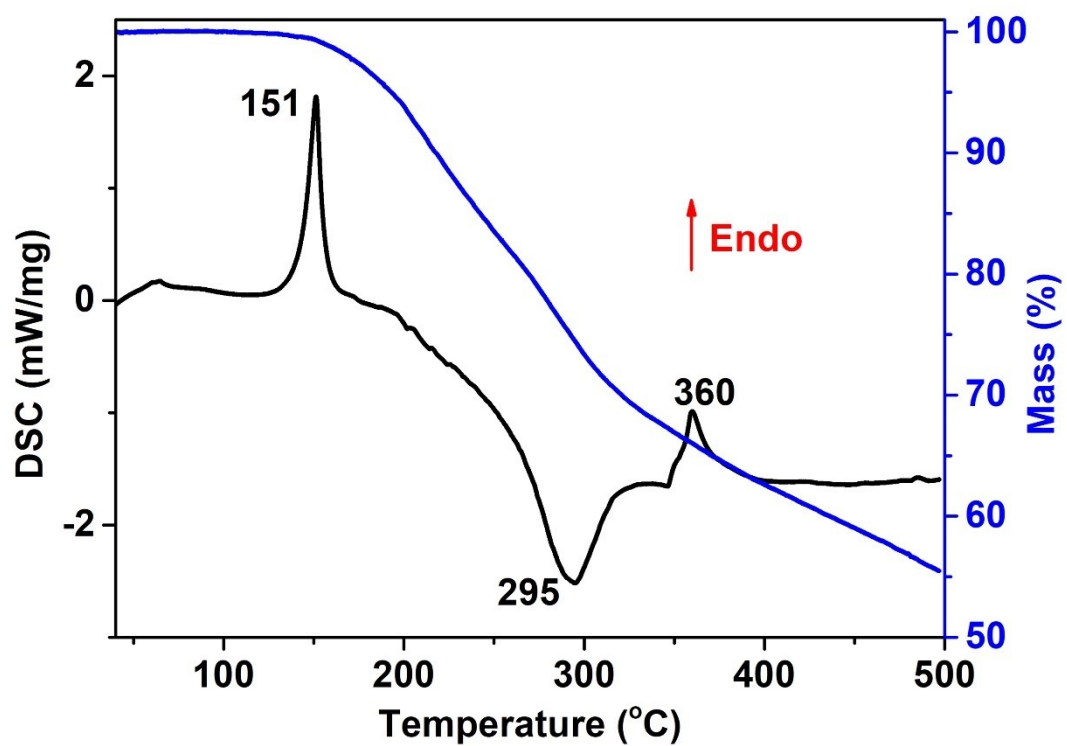


Figure S3. The UV-vis-NIR diffuse reflectance spectrum, inset gives the experimental band gap of $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$

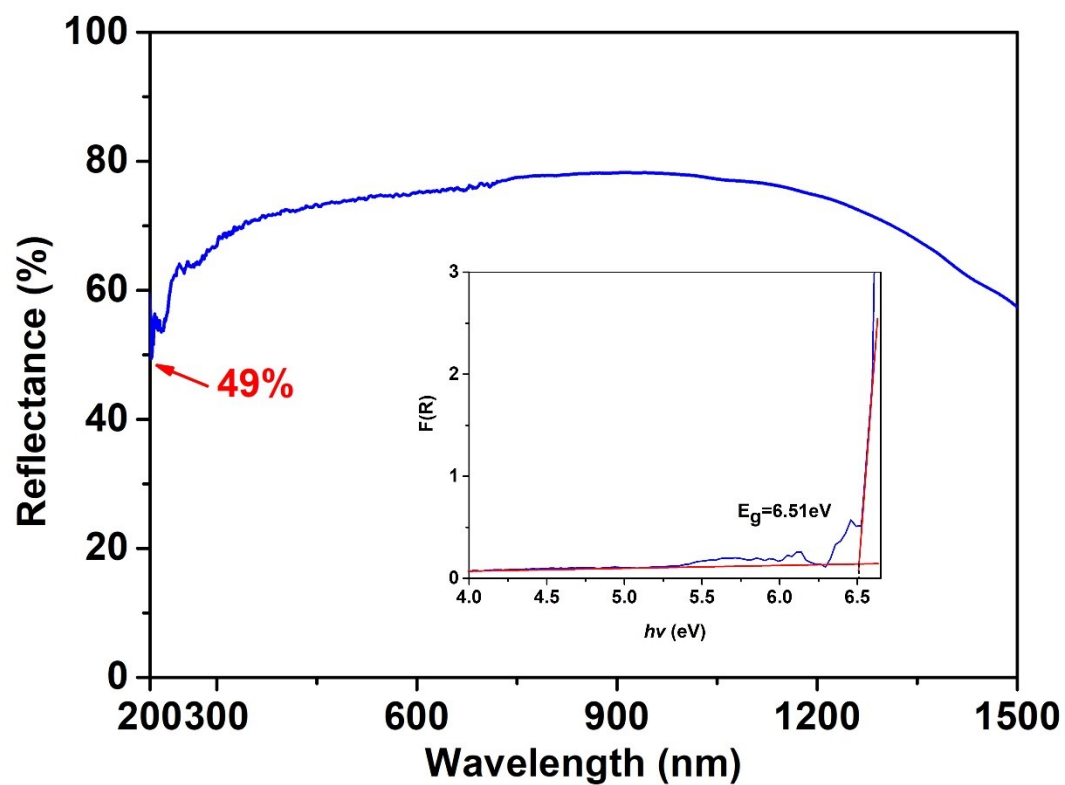


Figure S4. The IR spectrum of $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$.

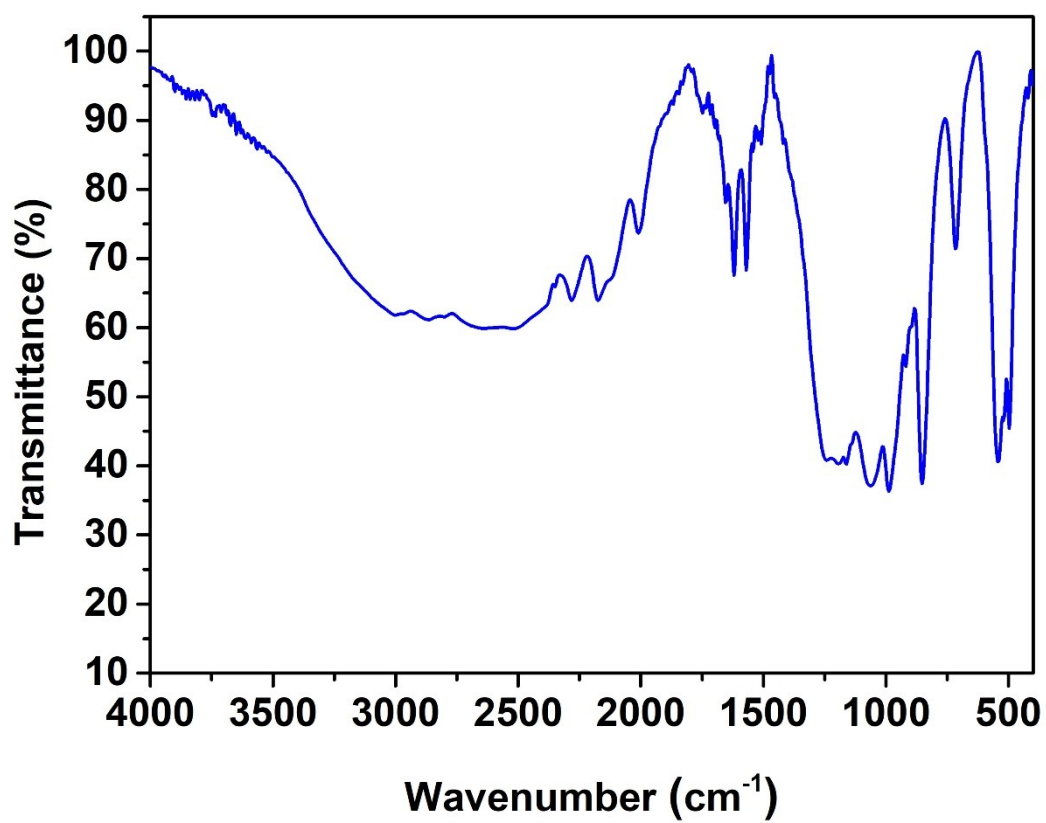


Figure S5. The band structure of $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$ with GGA method.

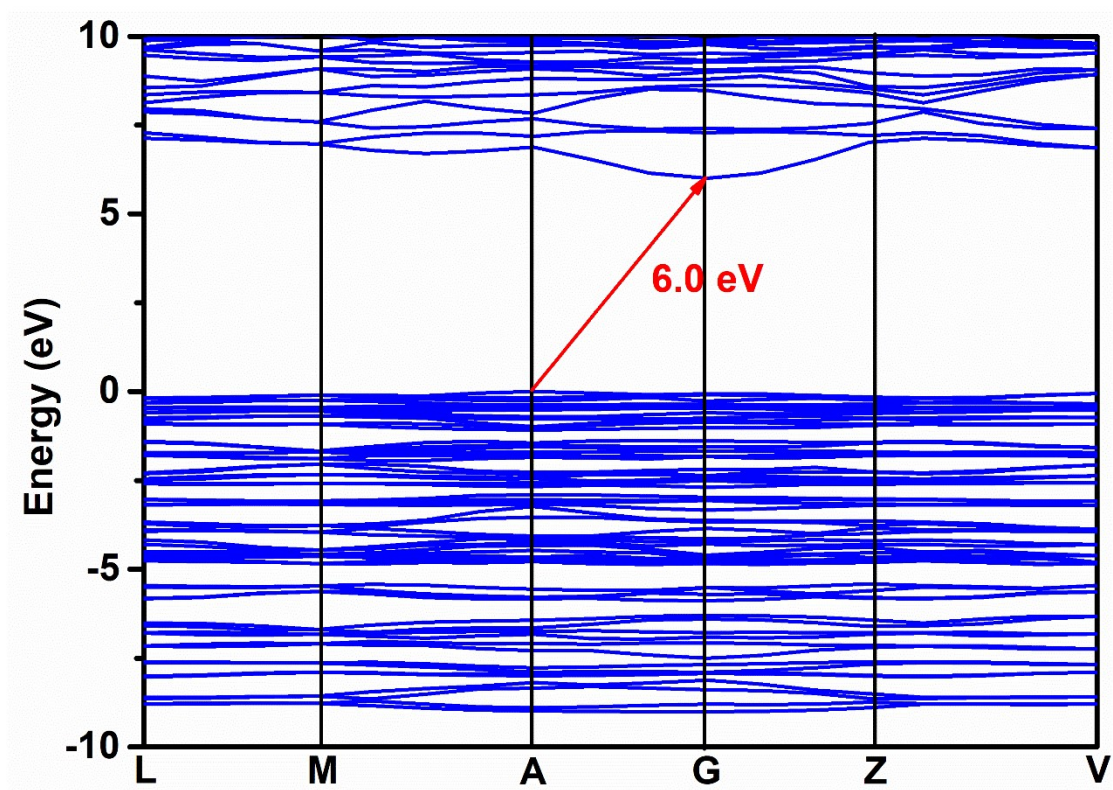


Table S1. Crystal data and structure refinement parameters of (N₂H₆)[HPO₃F]₂.

Empirical formula	(N ₂ H ₆)[HPO ₃ F] ₂
Formula weight	232.02
Temperature/K	300.0
Crystal system	monoclinic
Space group	<i>C2/c</i>
<i>a</i> /Å	14.1316(5)
<i>b</i> /Å	7.0340(2)
<i>c</i> /Å	7.9877(3)
α /°	90
β /°	96.763(3)
γ /°	90
Volume/Å ³	788.52(5)
<i>Z</i>	4
ρ_{calc} g/cm ³	1.954
μ /mm ⁻¹	5.545
<i>F</i> (000)	472.0
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	5.28 to 54.856
Index ranges	-16 $\leq h \leq$ 16, -8 $\leq k \leq$ 8, -9 $\leq l \leq$ 9
Reflections collected	5752
Independent reflections	727 [<i>R</i> _{int} = 0.0371, <i>R</i> _{sigma} = 0.0238]
Data/restraints/parameters	727/4/72
Goodness-of-fit on <i>F</i> ²	1.066
Final <i>R</i> indexes [<i>I</i> \geq 2 σ (<i>I</i>)] ^[a]	<i>R</i> ₁ = 0.0233, <i>wR</i> ₂ = 0.0658
Final <i>R</i> indexes (all data) ^[a]	<i>R</i> ₁ = 0.0250, <i>wR</i> ₂ = 0.0678
Largest diff. peak/hole (e/Å ³)	0.21/-0.27

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S2. Atomic coordinates equivalent isotropic displacement parameters and bond valence sum (BVS) for (N₂H₆)[HPO₃F]₂.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U _{eq} (Å ²)	BVS
N1	5511.1(10)	8363.0(19)	7593.0(17)	26.2(3)	-
P1	6397.7(3)	3130.8(5)	6927.4(5)	24.0(2)	5.066
O1	6075.0(10)	5027.9(16)	6283.5(15)	38.6(3)	1.952
O2	6213.9(12)	2746.0(19)	8752.8(15)	49.6(4)	2.288
O3	6058.7(9)	1442.0(15)	5908.9(13)	32.1(3)	1.912
F1	7495.0(9)	3141.2(17)	7024.9(19)	60.1(4)	0.961

Table S3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	35.1(8)	20.3(7)	23.0(7)	0.5(5)	2.7(6)	1.1(5)
P1	32.0(3)	18.8(3)	21.0(3)	-0.31(13)	2.64(17)	-1.46(13)
O1	62.7(8)	21.7(6)	32.2(6)	2.3(5)	8.4(6)	4.0(5)
O2	99.1(12)	27.9(7)	23.3(7)	-0.8(5)	12.9(7)	-6.5(7)
O3	49.8(7)	22.2(6)	23.8(6)	-1.6(4)	1.9(5)	-4.4(5)
F1	33.3(7)	63.4(8)	82.1(10)	-2.8(6)	0.3(6)	-4.2(5)

Table S4. Selected bond lengths for $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$.

P1-O1	1.4825(11)
P1-O2	1.5349(13)
P1-O3	1.4868(11)
P1-F1	1.5434(13)
N1-N1 ¹	1.435(3)

Symmetry transformations used to generate equivalent atoms:

#1 1-X, +Y, 3/2-Z

Table S5. Selected bond angles for (N₂H₆)[HPO₃F]₂.

Bond angles	
O1-P1-F1	106.23(7)
O2-P1-F1	103.55(9)
O3-P1-F1	106.77(7)
O1-P1-O2	114.12(7)
O1-P1-O3	117.59(7)
O2-P1-O3	107.41(7)

Table S6. Hydrogen bonds for (N₂H₆)[HPO₃F]₂.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2	H2	O1 ¹	0.901(18)	1.73(2)	2.5827(17)	156(3)
N1	H1A	O3 ²	0.878(16)	1.837(16)	2.7100(17)	173(2)
N1	H1B	O3 ¹	0.879(16)	1.796(17)	2.6740(18)	175(2)
N1	H1C	O1	0.876(15)	1.851(16)	2.7256(18)	177.1(19)

Symmetry transformations used to generate equivalent atoms:

#1 +X, 1-Y, 1/2+Z; #2 +X, 1+Y, +Z

Table S7. ^1H , ^{31}P and ^{19}F chemical shift parameters for $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$.

Type	δ (ppm)
^1H	9.23, 8.53
^{31}P	0.07, 3.06
^{19}F	-72.28, -78.34

Table S8. The reported optical properties of fluorophosphates.

Compounds	Birefringence	Band gap (eV)	Calculation method	Ref
(NH ₄) ₂ PO ₃ F	0.03@589.3 nm obv.	7.59	PBE0	6
Na ₂ PO ₃ F	0.028@1064 nm	6.14		
K ₂ PO ₃ F	0.021@1064 nm	6.79		
Rb ₂ PO ₃ F	0.02@1064 nm	6.76		
Cs ₂ PO ₃ F	0.018@1064 nm	6.94		
BaPO ₃ F	0.01@1064 nm	7.9		
K ₂ P ₂ O ₅ F ₂	0.023@1064 nm	7.74		
NaK ₃ (PO ₃ F) ₂	0.021@1064 nm	6.91		
KPO ₂ F ₂	0.047@1064 nm	7.95		
CsPO ₂ F ₂	0.045@1064 nm	7.99		
NH ₄ PO ₂ F ₂	0.046@1064 nm	8.15		
KHPO ₃ F	0.028@532 nm	6.92		
[C(NH ₂) ₃] ₂ PO ₃ F	0.039@532 nm	6.55	8	
NaNH ₄ PO ₃ F·H ₂ O	0.053@589.3 nm obv.	7.02	9	
LiPO ₂ F ₂	0.013@1064 nm	7.69	10	
KLa(PO ₂ F ₂) ₄	0.023@1064 nm	7.43	11	
NH ₄ La(PO ₂ F ₂) ₄	0.019@1064 nm	7.29	12	
(NH ₄) ₂ Ba(PO ₂ F ₂) ₄	0.022@1064 nm	6.87	This work	
SnPO ₃ F	0.075@1064 nm	4.83		
SrPO ₃ F	0.034@1064 nm	7.18		
(N ₂ H ₆)[HPO ₃ F] ₂	0.077@1064 nm	7.38	HSE06	This work
		8.13	PBE0	

Table S9. The real-space atom-cutting analysis of calculated birefringence in $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$. The cutting radius of N, P, O, F, and H were set as 0.75, 1.06, 0.73, 0.72 and 0.32

Cut unit	Δn (1064 nm)
None	0.077
$[\text{N}_2\text{H}_6]$	0.085
$[\text{HPO}_3\text{F}]$	0.015

References and Notes

1. SAINT, *Version 7.60A, Bruker Analytical X-ray Instruments, Inc., Madison, WI*, 2008.
2. Sheldrick, G. M. *SHELXTL, version 6.12; Bruker Analytical X-ray Instruments, Inc.: Madison, WI*, 2001.
3. A. L. Spek, *J. Appl. Crystallogr.* 2003, **36**, 7.
4. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. Probert, K. Refson, M. C. Payne, *Z. Kristallogr. Cryst. Mater.*, 2005, **220**, 567.
5. (a) A. M. Rappe, K. M. Rabe, E. Kaxiras, J. D. Joannopoulos, *Phys. Rev. B*, 1990, **41**, 1227; (b) J. S. Lin, A. Qteish, M. C. Payne, V. Heine, *Phys. Rev. B*, 1993, **47**, 4174; (c) M. H. Lee, PhD. Thesis, The University of Cambridge 1996.
6. B. B. Zhang, G. P. Han, Y. Wang, X. L. Chen, Z. H. Yang and S. L. Pan, *Chem. Mater.* **2018**, *30*, 5397-5403.
7. L. Xiong, J. Chen, J. Lu, C. Y. Pan and L. M. Wu, *Chem. Mater.* **2018**, *30*, 7823-7830.
8. J. Lu, J. N. Yue, L. Xiong, W. K. Zhang, L. Chen and L. M. Wu, *J. Am. Chem. Soc.* **2019**, *141*, 8093-8097.
9. G. P. Han, Y. Wang, H. Li, Z. H. Yang and S. L. Pan, *Chem. Commun.* **2019**, *55*, 1817-1820.
10. W. Y. Zhang, Z. L. Wei, Z. H. Yang and S. L. Pan, *Dalton Trans.* **2020**, *49*, 11591-11596.
11. W. Y. Zhang, W. Q. Jin, M. Cheng, R. N. Zhang, Z. H. Yang and S. L. Pan, *Dalton Trans.* **2021**, *50*, 10206-10213.
12. Y. Y. Qian, Q. Jing, H. M. Duan, M. H. Lee and H. B. Cao, *Phys. B* **2022**, 413676.