Tetrafluoroborate-Monofluorophosphate $(NH_4)_3[PO_3F][BF_4]$: First Member of Oxyfluoride with B-F and P-F Bonds

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1. Experimental Section

Crystal Growth. Single crystals of $(NH_4)_3[PO_3F][BF_4]$ were grown by a vapor-liquid diffusion method. In a plastic beaker, 10 g mixture of Na_2PO_3F, $(NH_4)HF_2$ and H_3BO_3 in the molar ratio of 1:3:1 was dissolved in 50 ml deionized water and stirred to make it completely clear, then single crystals of $(NH_4)_3[PO_3F][BF_4]$ crystallize at the bottom of beaker after several days.

Single Crystal Structure Data Collection. The single crystal diffraction data were collected on a Bruker D8 Venture Single Crystal X-ray Diffractometer (Mo Kα radiation with $\lambda = 0.71073$ Å) 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 Olex2.[2] No missed symmetry was proved using PLATON program.[3]

Characterization. Powder X-ray diffraction measurements for the targeted $(NH_4)_3[PO_3F][BF_4]$ were carried out on a Bruker D2 PHASER diffractometer equipped with Cu Kα radiation at room temperature. The 2θ range is 10-70 ° with a step size of 0.02 ° and a fixed counting time of 1 s/step. 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 $(NH_4)_3[PO_3F][BF_4]$ was placed in the Pt crucible, heated from 40 to 350 °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 $(NH_4)_3[PO_3F][BF_4]$ on a Shimadzu SolidSpec-3700DUV spectrophotometer. The polycrystalline powder of $(NH_4)_3[PO_3F][BF_4]$ 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, abound with CF_2

groups, was used as the external reference of ^{19}F chemical shifts, while boric acid solution at a specific concentration, that is 1mol·L^{-1}, was utilized as an external reference for ^{11}B chemical shifts. Meanwhile, the existence of B-F and P-F bonds was checked employing $^{31}P\{^{19}F\}$ and $^{11}B\{^{19}F\}$-REDOR NMR spectroscopy.

Computational Methods. The first-principles calculations were performed by the plane-wave pseudopotential method implemented in the CASTEP package.[4] The exchange correlation interaction was treated by the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional.[5,6] To achieve energy convergence, the kinetic energy cutoff of 850 eV for $(NH_4)_3[PO_3F][BF_4]$ within normal-conserving pseudopotential (NCP) was adopted.[7] The Monkhorst-Pack k-point meshes in the Brillouin zone was set as 3 × 4 × 3 for $(NH_4)_3[PO_3F][BF_4]$.

2. Tables and Figures.

Table S1. Crystal data and structure refinement for $(NH_4)_3[PO_3F][BF_4]$.

Empirical formula	$(NH_4)_3[PO_3F][BF_4]$
Formula weight	238.91
Temperature/K	300.15
Crystal system	monoclinic
Space group	$P2_1/m$
a/Å	7.8384(7)
b/Å	6.0996(6)
c/Å	9.9079(9)
α/°	90.00
β/°	111.990(3)
γ/°	90.00
Volume/Å^3	439.24(7)
Z	2
ρ_{calc}g/cm^3	1.806
μ/mm^{-1}	0.382
F(000)	244.0
Crystal size/mm^3	0.145 × 0.134 × 0.105
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4.44 to 55.06
Index ranges	$-10 \le h \le 10$, $-7 \le k \le 7$, $-12 \le l \le 12$
Reflections collected	9147
Independent reflections	1101 [R_{int} = 0.0774, R_{sigma} = 0.0363]
Data/restraints/parameters	1101/27/103
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)][a]	R_1 = 0.0501, wR_2 = 0.1061
Final R indexes [all data][a]	R_1 = 0.0663, wR_2 = 0.1147
Largest diff. peak/hole / e Å^{-3}	0.42/-0.36

[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 $(NH_4)_3[PO_3F][BF_4]$.

Atom	*x*	*y*	*z*	U(eq)	BVS
N1	2851(5)	2500	7600(4)	35.2(8)	-
N2	-1424(5)	2500	-262(4)	36.3(8)	-
N3	3462(5)	-2500	4346(4)	41.0(8)	-
P1	4088.2(13)	2500	1634.2(10)	25.4(3)	5.31
B1	529(6)	2500	3622(5)	39.1(10)	3.00
O1	2382(4)	2500	318(3)	66.2(11)	1.83
O2	4393(4)	464(4)	2488(3)	78.0(10)	1.81
F1	5665(3)	2500	988(3)	44.7(6)	0.87
F2	191(3)	635(3)	2744(2)	60.8(6)	0.73
F3	2357(4)	2500	4561(3)	60.1(8)	0.75
F4	-588(5)	2500	4425(4)	90.9(12)	0.75

Table S3. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $(NH_4)_3[PO_3F][BF_4]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	33.6(18)	42(2)	32.3(17)	0	14.5(15)	0
N2	30.0(17)	31.3(18)	45(2)	0	11.2(15)	0
N3	42(2)	43(2)	38(2)	0	14.6(17)	0
P1	24.8(5)	27.4(5)	25.2(5)	0	10.9(4)	0
B1	31(2)	50(3)	36(2)	0	13(2)	0
O1	27.0(16)	140(4)	29.6(15)	0	7.9(13)	0
O2	94(2)	66.3(17)	106(2)	59.7(16)	74.5(19)	46.2(15)
F1	31.6(12)	65.4(17)	45.1(13)	0	23.3(11)	0
F2	66.8(13)	50.9(12)	56.2(11)	-5.6(9)	13.3(10)	-8.6(10)
F3	40.0(15)	88(2)	43.0(14)	0	5.3(12)	0
F4	76(2)	126(3)	98(3)	0	64(2)	0

Table S4. Bond lengths for $(NH_4)_3[PO_3F][BF_4]$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O1	1.478(3)	B1	F2	1.396(3)
P1	O2[1]	1.471(2)	B1	F2[1]	1.396(3)
P1	O2	1.471(2)	B1	F3	1.385(5)
P1	F1	1.590(2)	B1	F4	1.386(5)

Table S5. The bond angles of $(NH_4)_3[PO_3F][BF_4]$.

Bond angles		Bond angles	
O1-P1-F1	103.15(15)	F2-B1-F2	109.2(3)
O2-P1-O1	113.97(14)	F3-B1-F2	109.0(2)
O2-P1-O1	113.97(14)	F3-B1-F2	109.0(2)
O2-P1-O2	115.2(2)	F3-B1-F4	109.3(4)
O2-P1-F1	104.37(11)	F4-B1-F2	110.1(2)
O2-P1-F1	104.36(11)	F4-B1-F2	110.1(2)

Table S6. Hydrogen bonds for $(NH_4)_3[PO_3F][BF_4]$.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	O1[1]	0.956(13)	1.896(13)	2.851(4)	177(4)
N1	H2	O2[2]	0.949(12)	1.961(17)	2.844(3)	154(3)
N2	H5	O1	0.967(13)	1.874(18)	2.819(4)	165(4)
N2	H4	F2[3]	0.965(13)	2.20(2)	2.990(4)	139(3)
N2	H4	F2	0.965(13)	2.20(2)	2.990(4)	139(3)
N2	H6	O1[4]	0.955(13)	2.30(3)	3.1364(11)	147(3)
N2	H6	O2[5]	0.955(13)	2.28(2)	3.115(4)	145(3)
N3	H7	F4[6]	0.967(13)	2.09(3)	2.935(5)	145(4)
N3	H9	O2	0.955(12)	1.973(17)	2.863(4)	154(3)
N3	H8	O2[7]	0.956(13)	2.359(15)	3.203(5)	146.9(12)
N3	H8	O2[2]	0.956(13)	2.359(15)	3.203(5)	146.9(12)

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

#5 -X,-Y,-Z #6 -X,-1/2+Y,1-Z #7 1-X,-1/2+Y,1-Z

Table S7. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for $(NH_4)_3[PO_3F][BF_4]$.

Atom	*x*	*y*	*z*	U(eq)
H1	2640(50)	2500	8490(30)	59(14)
H3	1670(30)	2500	6810(30)	100(20)
H2	3460(40)	1200(40)	7500(30)	83(13)
H5	-180(30)	2500	-250(50)	69(16)
H4	-1290(70)	2500	750(20)	120(30)
H6	-1970(50)	1140(40)	-690(40)	120(18)
H7	2220(30)	-2500	4320(60)	110(20)
H9	3580(50)	-1210(40)	3850(30)	99(15)
H8	4280(60)	-2500	5340(20)	110(20)

Figure S1. The experimental and calculated PXRD patterns of $(NH_4)_3[PO_3F][BF_4]$.

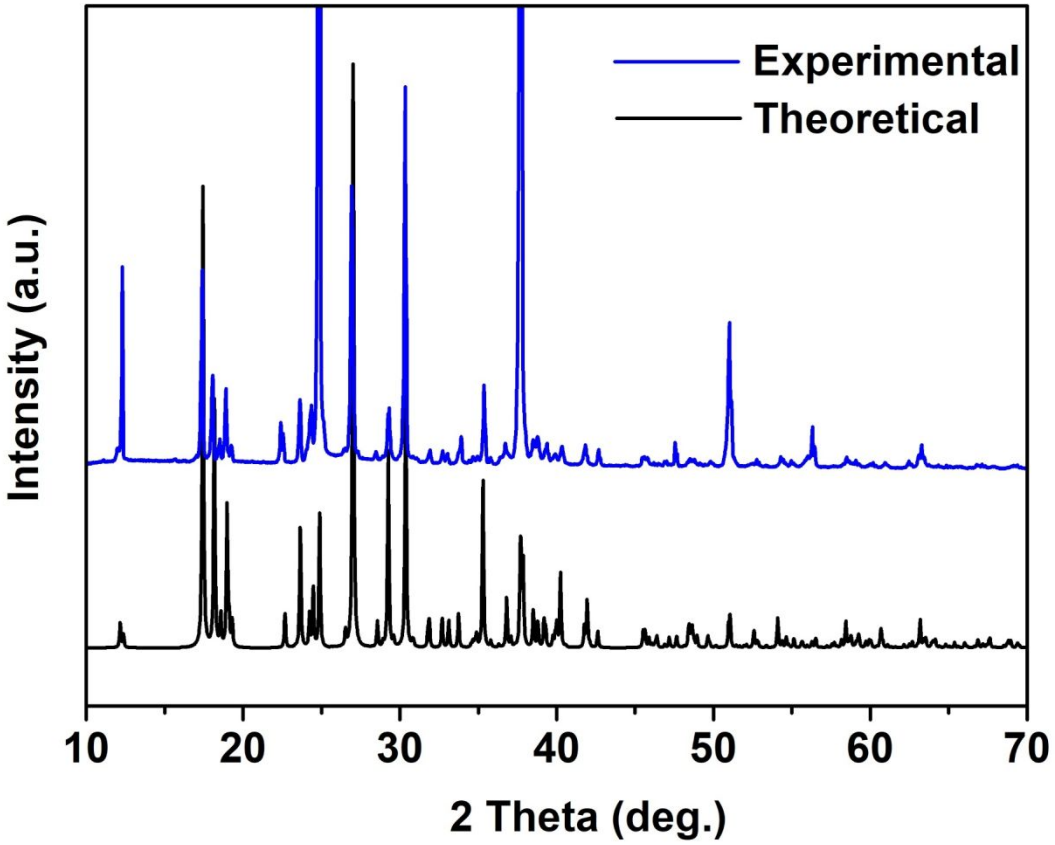


Figure S2. Rietveld refinement of the powder XRD profile of $(NH_4)_3[PO_3F][BF_4]$.

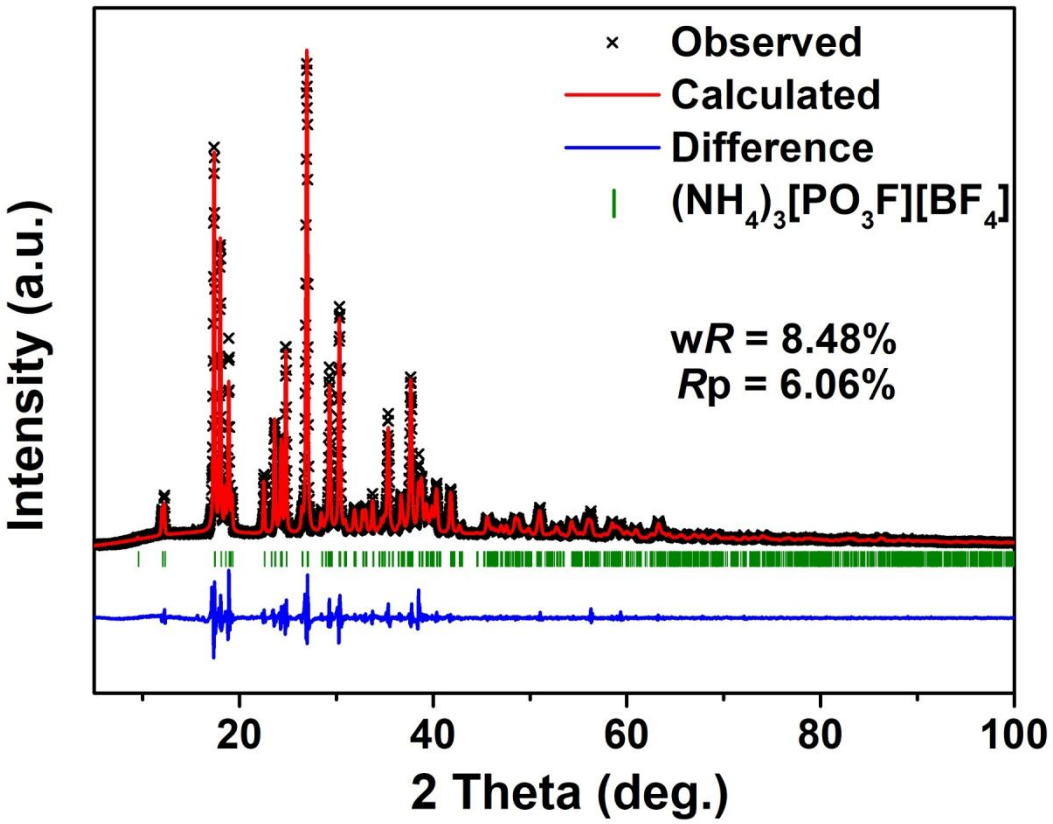


Figure S3. The energy-dispersive X-ray spectroscopy of $(NH_4)_3[PO_3F][BF_4]$.

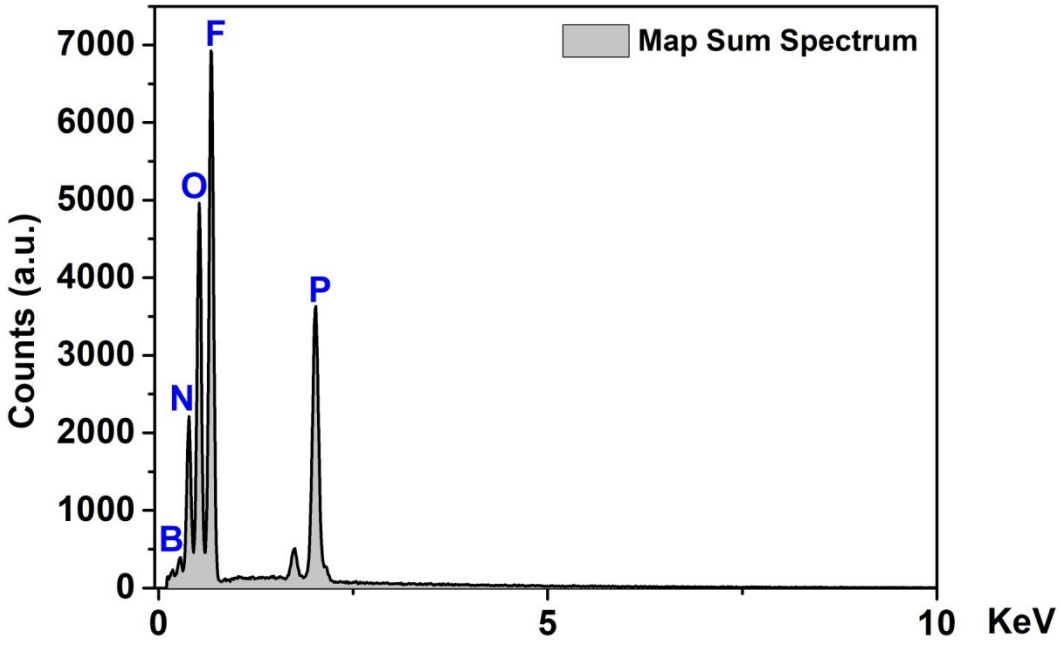


Figure S4. The IR spectrum of $(NH_4)_3[PO_3F][BF_4]$.

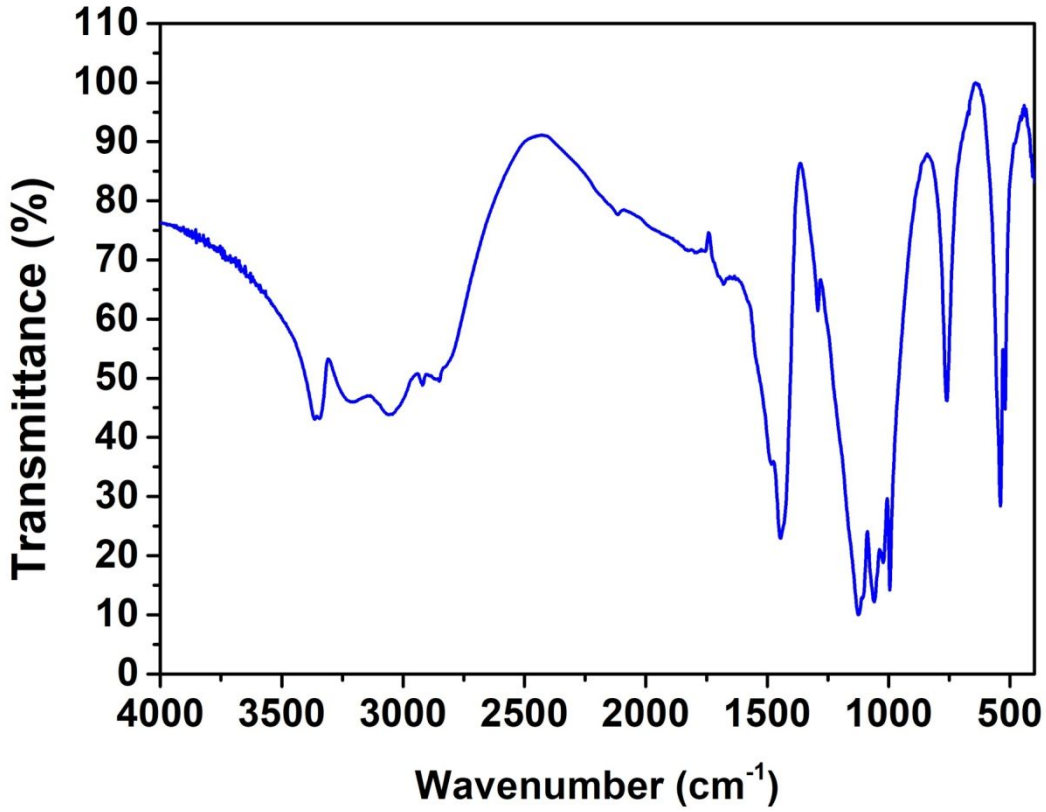


Figure S5. The TG and DSC curves of $(NH_4)_3[PO_3F][BF_4]$.

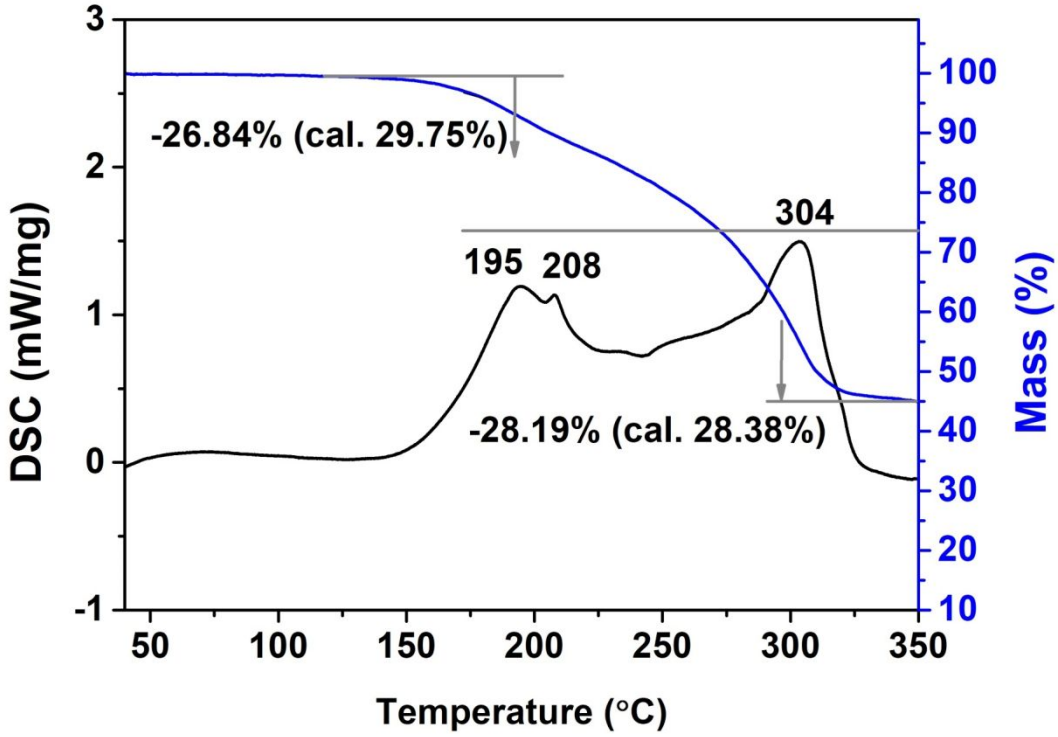


Figure S6. The UV-vis-NIR diffuse reflectance spectrum of $(NH_4)_3[PO_3F][BF_4]$.

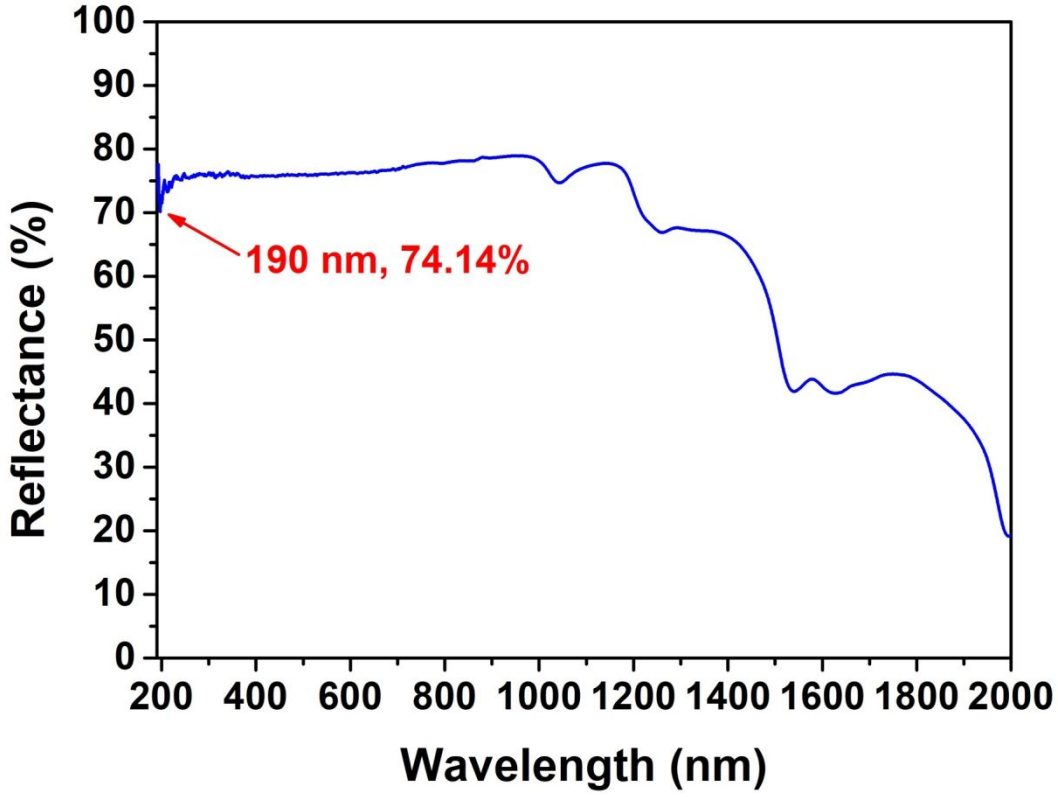
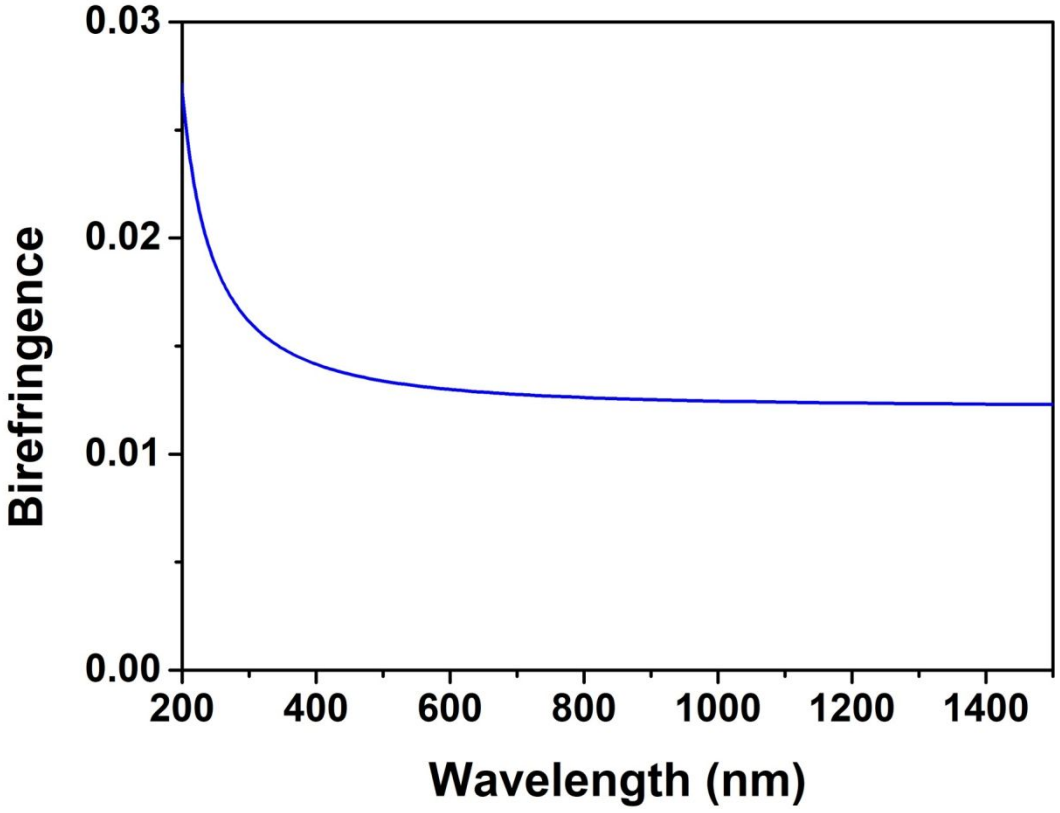


Figure S7. The birefringence curve of $(NH_4)_3[PO_3F][BF_4]$.



References and Notes

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