Supporting Information

Synergistic Dual-Modification Strategy of π-Conjugated Cations and Tetrahedra: Rational Design of Ultraviolet High-Birefringence Monofluorophosphates

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Experimental Procedures

Synthesis

All of the chemicals were of analytical grade from commercial sources and used without further purification. $CH_6N_4{\cdot}H_2CO_3$ (Aladdin, 98.5%), HCl (AR), Na_2PO_3F (Macklin, 98 %), C_3H_6O (99 %), and HF were purchased from Macklin.

Two compounds were synthesized at room temperature without additional heating. The millimeter-sized single crystals of $(CN_4H_7)_2PO_3F{\cdot}H_2O$ and $(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$ were obtained by the solution volatilization method.

Growth of $(CN_4H_7)_2PO_3F{\cdot}H_2O$ crystals by evaporation method:

(a) A solution was prepared by adding $CH_6N_4{\cdot}H_2CO_3$ (10 mmol) and 10 mL of distilled water to a 250 mL plastic beaker, followed by the slow addition of HF solution to induce CO_2 gas evolution. This mixture was designated as Solution A.

(b) Na_2PO_3F (5 mmol) was added to Solution A, and the mixture was stirred thoroughly to ensure homogeneity.

(c) The crystals were isolated from the mother liquor following natural evaporation, with care taken to prevent complete evaporation of the solution.

Growth of $(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$ crystals by evaporation method:

(a) A solution was prepared by adding $CH_6N_4{\cdot}H_2CO_3$ (10 mmol) and 20 mL of distilled water to a 250 mL plastic beaker, followed by the slow addition of HCl solution to induce CO_2 gas evolution. This mixture was designated as Solution B.

(b) Na_2PO_3F (5 mmol) and 100 ml C_3H_6O were added to Solution B, and the mixture was stirred thoroughly to ensure homogeneity.

(c) The crystals were isolated from the mother liquor following natural evaporation, with care taken to prevent complete evaporation of the solution.

Structural Determination

To perform the structural characterization of the as-synthesized samples, plate-shaped single crystals with suitable sizes of the title compounds were selected under an optical microscope. Single-crystal X-ray diffraction data of the two compounds were collected on a Bruker D8 Venture diffractometer assembled with monochromatic Mo-Kα (λ = 0.71073 Å) as the radiation source. By using the Bruker SAINT program, data integration was performed.[1] The structure of the two crystals was determined by the direct method and refined through the SHELXTL system using Olex2 software.[2,3] The positions of all the atoms were refined by full matrix least-squares techniques. The PLATON program was used to confirm the above structures as no higher symmetry was recommended.[4]

Powder X-ray Diffraction

The purity of polycrystalline powder samples of the two compounds was confirmed using the Bruker D2 PHASER X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å), and the diffraction data were collected in the 2θ range from 5 to 50 ° (step size: 0.02 °), respectively.

Spectral Analysis

The infrared (IR) absorption spectra were measured to confirm the presence of the anionic units of $(CN_4H_7)_2PO_3F{\cdot}H_2O$ and $(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$ on a SHIMADZU IR-Affinity-1 Fourier Transform IR spectrometer in the range of 400−4000 cm^{-1}. Polycrystalline powders of the two compounds were mixed with dried KBr in a mass ratio of 1:100 to prepare the samples tested. To determine the cutoff edge of $(CN_4H_7)_2PO_3F{\cdot}H_2O$ and $(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$, UV-vis-NIR transmittance spectra were measured by a Shimadzu SolidSpec-3700DUV spectrophotometer at room temperature.

Computational Details and Methods

The electronic structures as well as optical properties of $(CN_4H_7)_2PO_3F{\cdot}H_2O$ and $(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$ were determined employing the CASTEP package based on density functional theory (DFT) with the norm-conserving pseudopotentials (NCP).[5,6] The functionals developed by Perdew-Burke-Ernzerhof (PBE) in generalized gradient approximation (GGA)[7] form were adopted to model the exchange-correlation terms in the Hamiltonian. The plane-wave energy cutoff of $(CN_4H_7)_2PO_3F{\cdot}H_2O$ and $(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$ was set at 850 and 940 eV. Self-consistent field (SCF) calculations were performed with a convergence criterion of 10^{-6} and 5.0×10^{-6} eV/atom on the total energy. The k-points of the Monkhorst-Pack grid used in the calculation of $(CN_4H_7)_2PO_3F{\cdot}H_2O$ and $(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$ are 5 × 1 × 2 and 5 × 4 × 3. Besides, the contribution of planar π-conjugated cations, $[PO_3F]$, and $[H_2O]$ units to the birefringence of $(CN_4H_7)_2PO_3F{\cdot}H_2O$ and $(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$ were further investigated using the real space atom-cutting method. The cutting radii of C, N, O, P, F, and H were set as 0.77, 0.75, 0.73, 1.06, 0.72, and 0.32 Å, respectively.

The HOMO–LUMO gap, energy level, and polarizability anisotropy of functional units were calculated using DFT implemented by the Gaussian09 package.[8] The B3LYP (Becke, three-parameter, Lee–Yang–Parr) exchange-correlation functional with the Lee–Yang–Parr correlation functional at the 6-31G+ and 6-31G++ basis set in Gaussian was employed.

The linear optical properties of title compounds including the dielectric function $\varepsilon(\omega)$ is obtained based on the following equations[9-11]:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (1)$$

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{\Omega}\lim_{q\to 0}\frac{1}{q^2} \times \sum_{c,v,k} 2\omega_k \delta(E_c - E_k - \omega)|\langle c \mid e{\cdot}q \mid v\rangle|^2 \quad (2)$$

where, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and the imaginary part of the dielectric function, respectively. According to the formula (2), $\varepsilon_2(\omega)$ is determined by the integrated optical transitions $|\langle c \mid e{\cdot}q \mid v\rangle|$ from the valence states (v) to the conduction states (c), and e, q denotes the polarization direction of the photon and the electron momentum operator, respectively. The real part of the dielectric function $\varepsilon_1(\omega)$ can be obtained from the imaginary part of the dielectric function $\varepsilon_2(\omega)$ based on the Kramers-Kronig transformation[12]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\Omega \varepsilon_2(\Omega)}{\Omega^2 - \omega^2} d\Omega \quad (3)$$

Then the refractive index $n(\omega)$ (and the birefringence Δn) can be calculated by using the following equation:

$$n(\omega) = \frac{1}{\sqrt{2}} \left\{ \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2} + \varepsilon_1(\omega) \right] \right\}^{\frac{1}{2}} \quad (4)$$

Table S1. Crystal data and structure refinement for $(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$.

Formula	$(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$
Formula weight	346.32
Temperature / K	298
Crystal system	Triclinic
Space group	$P\bar{1}$
a / Å	7.3372(6)
b / Å	9.0541(8)
c / Å	12.6489(10)
α / °	96.383(3)
β / °	96.496(3)
γ / °	97.670(3)
Volume / Å^3	820.59(12)
Z	2
ρ_{calc} g/cm^3	1.402
μ / mm^{-1}	0.208
F (000)	368.0
Radiation	Mo K*α* (*λ* = 0.71073)
2*θ* range for date collection/ °	3.268 to 50.678
Index ranges	$-8 \le h \le 8$, $-10 \le k \le 10$, $-15 \le l \le 15$
Reflections collected	11366
Independent reflections	2990 [R_{int} = 0.0371, R_{sigma} = 0.0333]
Completeness (%)	99.9
Data/restraints/parameters	2990 / 1 / 216
Goodness-of-fit on F^2	1.042
Final *R* indices [$I \ge 2\sigma(I)$][a]	R_1= 0.0398, wR_2= 0.1072
Final *R* indices (all data)[a]	R_1= 0.0461, wR_2= 0.1130
Largest diff. peak/hole /e Å^{-3}	0.34 / - 0.34

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

Table S2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 ×10^3) for $(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$. *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	*U*(eq)
C(1)	5919(3)	4419(2)	8581(2)	29(1)
C(2)	3431(4)	1032(3)	10735(2)	54(1)
C(3)	3122(3)	1986(2)	9862(2)	34(1)
C(4)	1210(3)	1850(3)	9303(3)	57(1)
C(5)	2011(3)	-2853(2)	4489(2)	34(1)
C(6)	4092(4)	363(3)	7004(2)	55(1)
C(7)	3213(3)	698(2)	5956(2)	40(1)
C(8)	3113(4)	2301(3)	5815(2)	56(1)
N(1)	7509(2)	4119(2)	9038(1)	40(1)
N(2)	5862(2)	5308(2)	7824(1)	35(1)
N(3)	4335(2)	3761(2)	8870(1)	31(1)
N(4)	4545(2)	2838(2)	9675(1)	34(1)
N(5)	1988(3)	-4261(2)	4690(2)	43(1)
N(6)	1521(3)	-2542(2)	3514(1)	43(1)
N(7)	2595(3)	-1778(2)	5309(1)	38(1)
N(8)	2535(2)	-284(2)	5158(1)	38(1)
P(1)	1093(1)	6262(1)	7651(1)	29(1)
O(1)	949(2)	4844(2)	8167(1)	48(1)
O(2)	2673(2)	6460(2)	7002(1)	40(1)
O(3)	-739(2)	6508(2)	7092(1)	37(1)
O(4)	-942(4)	-500(2)	6886(2)	85(1)
F(1)	1576(2)	7572(2)	8608(1)	60(1)

Table S3. Bond lengths [Å] and angles [deg] for $(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$.

C(1)-N(1)	1.317(2)	C(6)-C(7)	1.488(3)
C(1)-N(2)	1.318(2)	C(7)-C(8)	1.493(3)
C(1)-N(3)	1.341(2)	C(7)-N(8)	1.275(3)
C(2)-C(3)	1.491(3)	N(3)-N(4)	1.396(2)
C(3)-C(4)	1.482(3)	N(7)-N(8)	1.392(2)
C(3)-N(4)	1.273(3)	P(1)-O(1)	1.5007(15)
C(5)-N(5)	1.326(3)	P(1)-O(2)	1.4969(14)
C(5)-N(6)	1.316(3)	P(1)-O(3)	1.5022(14)
C(5)-N(7)	1.331(3)	P(1)-F(1)	1.5710(14)
C(1)-N(3)-N(4)	115.40(15)	N(2)-C(1)-N(3)	119.86(17)
C(2)-C(3)-C(4)	117.23(19)	N(5)-C(5)-N(6)	121.1(2)
C(2)-C(3)-N(4)	116.09(19)	N(5)-C(5)-N(7)	116.96(18)
C(3)-N(4)-N(3)	118.55(16)	N(6)-C(5)-N(7)	121.93(18)
C(4)-C(3)-N(4)	126.68(19)	C(6)-C(7)-N(8)	125.0(2)
C(5)-N(7)-N(8)	119.32(17)	O(1)-P(1)-O(2)	113.99(9)
C(6)-C(7)-C(8)	118.2(2)	O(1)-P(1)-O(3)	112.40(8)
C(7)-N(8)-N(7)	116.31(18)	O(1)-P(1)-F(1)	105.18(10)
C(8)-C(7)-N(8)	116.9(2)	O(2)-P(1)-O(3)	114.62(8)
N(1)-C(1)-N(2)	121.17(17)	O(2)-P(1)-F(1)	104.89(9)
N(1)-C(1)-N(3)	118.94(17)	O(3)-P(1)-F(1)	104.48(8)

Table S4. Hydrogen bonds for $(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$.

D−H···A	d(D−H)/Å	d(H···A)/Å	d(D···A)/Å	D−H···A/º
N(1)-H(1)...O(1)#1	0.88	2.04	2.891(2)	164.1
N(2)-H(3)...O(3)#1	0.88	2.00	2.877(2)	176.4
N(2)-H(4)...O(2)	0.88	1.97	2.826(2)	165.1
N(3)-H(5)...O(1)	0.88	2.02	2.875(2)	162.4
N(5)-H(14)...O(3)#3	0.88	1.97	2.842(2)	173.5
N(5)-H(15)...O(2)#2	0.88	2.14	2.897(2)	144.0
N(6)-H(12)...O(1)#3	0.88	2.23	3.047(3)	153.5
N(6)-H(13)...O(4)#3	0.88	2.07	2.932(3)	166.7
N(7)-H(16)...O(2)#2	0.88	2.05	2.810(2)	144.4
O(4)-H(24)...O(3)#2	0.99	2.13	2.772(2)	121.0
O(4)-H(23)...N(8)#3	0.73	2.37	2.916(3)	132.7

Symmetry transformations used to generate equivalent atoms:
#1 x+1, y, z; #2 x, y-1, z; #3 -x,-y,-z+1

Table S5. Crystal data and structure refinement for $(CN_4H_7)_2PO_3F{\cdot}H_2O$.

Formula	$(CN_4H_7)_2PO_3F{\cdot}H_2O$
Formula weight	266.20
Temperature / K	298
Crystal system	Monoclinic
Space group	$P2_1/c$
a / Å	4.9572(6)
b / Å	20.492(3)
c / Å	11.0338(16)
β / °	91.685(5)
Volume / Å^3	1120.4(3)
Z	4
ρ_{calc} g/cm^3	1.578
μ / mm^{-1}	0.279
F (000)	560
Radiation	Mo Kα (λ = 0.71073)
2θ range for date collection/ °	3.976 to 50.694
Index ranges	$-5 \le h \le 5$, $-24 \le k \le 24$, $-13 \le l \le 13$
Reflections collected	9709
Independent reflections	2040 [R_{int} = 0.0487, R_{sigma} = 0.0346]
Completeness (%)	99.9
Data/restraints/parameters	2040 / 0 / 150
Goodness-of-fit on F^2	1.049
Final R indices [$I \ge 2\sigma(I)$][a]	R_1= 0.0349, wR_2= 0.0863
Final R indices (all data)[a]	R_1= 0.0445, wR_2= 0.0929
Largest diff. peak/hole /e Å^{-3}	0.18 / - 0.30

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

Table S6. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 ×10^3) for $(CN_4H_7)_2PO_3F{\cdot}H_2O$. *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	*U*(eq)
C(1)	4301(4)	7945(1)	3473(2)	33(1)
C(2)	4333(4)	4577(1)	3096(2)	30(1)
N(1)	6481(4)	4827(1)	3674(2)	38(1)
N(2)	3080(4)	4068(1)	3556(2)	41(1)
N(3)	3475(4)	4839(1)	2064(2)	34(1)
N(4)	1239(4)	4561(1)	1425(2)	34(1)
N(5)	6394(4)	7643(1)	3999(2)	48(1)
N(6)	3169(4)	8445(1)	4007(2)	43(1)
N(7)	3405(4)	7729(1)	2406(2)	37(1)
N(8)	1263(4)	8050(1)	1786(2)	35(1)
P(1)	8022(1)	6290(1)	1812(1)	25(1)
O(1)	7698(3)	6204(1)	3160(1)	36(1)
O(2)	7234(3)	6954(1)	1363(1)	38(1)
O(3)	6964(3)	5737(1)	1053(1)	41(1)
O(4)	12684(3)	6168(1)	4416(1)	46(1)
F(1)	11184(2)	6267(1)	1653(1)	43(1)

Table S7. Bond lengths [Å] and angles [deg] for $(CN_4H_7)_2PO_3F{\cdot}H_2O$.

C(1)-N(5)	1.327(3)	N(3)-N(4)	1.416(2)
C(1)-N(6)	1.317(3)	N(7)-N(8)	1.409(2)
C(1)-N(7)	1.322(3)	P(1)-O(1)	1.5109(14)
C(2)-N(1)	1.328(3)	P(1)-O(2)	1.4972(15)
C(2)-N(2)	1.323(3)	P(1)-O(3)	1.4944(15)
C(2)-N(3)	1.319(3)	P(1)-F(1)	1.5828(13)
C(1)-N(7)-N(8)	120.28(17)	N(6)-C(1)-N(7)	121.5(2)
C(2)-N(3)-N(4)	119.55(17)	O(1)-P(1)-O(2)	113.40(9)
N(1)-C(2)-N(2)	119.94(19)	O(1)-P(1)-O(3)	114.68(9)
N(1)-C(2)-N(3)	119.41(19)	O(1)-P(1)-F(1)	103.91(8)
N(2)-C(2)-N(3)	120.65(19)	O(2)-P(1)-O(3)	114.83(9)
N(5)-C(1)-N(6)	120.3(2)	O(2)-P(1)-F(1)	103.86(8)
N(5)-C(1)-N(7)	118.14(19)	O(3)-P(1)-F(1)	104.38(8)

Table S8. Hydrogen bonds for $(CN_4H_7)_2PO_3F{\cdot}H_2O$.

D−H···A	d(D−H)/Å	d(H···A)/Å	d(D···A)/Å	D−H···A/º
N(1)-H(1)...O(1)	0.88	2.15	2.945(2)	149.7
N(1)-H(2)...O(4)#5	0.88	2.16	2.952(2)	149.7
N(2)-H(3)...O(4)#5	0.88	2.31	3.062(2)	144.1
N(2)-H(4)...N(8)#6	0.88	2.27	3.013(3)	142.3
N(3)-H(5)...O(3)	0.88	1.93	2.781(2)	161.4
N(4)-H(7)...O(3)#2	0.89	2.08	2.964(2)	172.7
N(5)-H(8)...O(1)	0.88	2.34	3.163(3)	155.3
N(5)-H(9)...O(2)#9	0.88	1.91	2.756(2)	161.7
N(6)-H(10)...F(1)#8	0.88	2.55	3.163(2)	127.5
N(6)-H(11)...N(4)#7	0.88	2.40	3.189(3)	148.9
N(7)-H(12)...O(2)	0.88	1.95	2.752(2)	150.5
N(8)-H(13)...O(2)#4	0.89	2.15	3.032(2)	168.0
N(8)-H(14)...O(4)#3	0.89	2.29	3.164(3)	167.0
O(4)-H(15)...F(1)	0.87	2.58	3.123(2)	121.3
O(4)-H(15)...O(1)	0.87	1.93	2.799(2)	174.5
O(4)-H(16)...O(1)#1	0.87	2.05	2.882(2)	160.3

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z #2 -x+1,-y+1,-z #3 x-1,-y+3/2,z-1/2
#4 x-1,y,z #5 -x+2,-y+1,-z+1 #6 -x,y-1/2,-z+1/2
#7 -x,y+1/2,-z+1/2 #8 x-1,-y+3/2,z+1/2 #9 x,-y+3/2,z+1/2

Table S9. Comparison of the optical properties of monofluorophosphates and difluorophosphates.

	Compound	Space group	Cutoff edge (nm)	Birefringence	Ref.
1	$(C_4N_4H_{11})_2PO_3F·H_2O$	$P\bar{1}$	267[b]	0.165 @ 546 nm[d]	This work
2	$(CN_4H_7)_2PO_3F·H_2O$	$P2_1/c$	214[b]	0.116 @ 546 nm[d]	This work
3	$K_3Sc_3(PO_4)(PO_3F)_2F_5$	Cc	200[a]	0.026 @ 546 nm[d]	13
4	$Cd_{2.5}(NH_4)_2(PO_3F)_3Cl·2H_2O$	$P2_1/c$	215[a]	0.012 @ 546 nm[e]	14
5	$(NH_4)_2PO_3F$	$Pna2_1$	177[b]	0.027 @ 1064 nm[d]	15
6	Na_2PO_3F	$P2_12_12_1$	202[c]	0.028 @ 1064 nm[d]	15
7	K_2PO_3F	$Pnma$	183[c]	0.021 @ 1064 nm[d]	15
8	Rb_2PO_3F	$Pnma$	183[c]	0.020 @ 1064 nm[d]	15
9	Cs_2PO_3F	$Pnma$	179[c]	0.018 @ 1064 nm[d]	15
10	$BaPO_3F$	$P2_1/c$	159[c]	0.010 @ 1064 nm[d]	15
11	$NaK_3(PO_3F)_2$	$P\bar{3}m1$	179[c]	0.021 @ 1064 nm[d]	15
12	$K_2P_2O_5F_2$	$C2/c$	160[c]	0.023 @ 1064 nm[d]	15
13	$NaNH_4PO_3F·H_2O$	Pn	176[b]	0.035 @ 532 nm[d]	16
14	$KHPO_3F$	$P2_1$	179[c]	0.028 @ 532 nm[d]	16
15	$[C(NH_2)_3]_2PO_3F$	Cm	194[b]	0.039 @ 532 nm[d]	16
16	$(NH_4)_3[PO_3F][BF_4]$	$P2_1/m$	190[a]	0.012 @ 1064 nm[d]	17
17	α-$Cd(NH_4)_2(PO_3F)_2·2H_2O$	$P2_1/n$	200[a]	0.015 @ 546 nm[e]	18
18	β-$Cd(NH_4)_2(PO_3F)_2·2H_2O$	$Cmc2_1$	200[a]	0.026 @ 546 nm[e]	18
19	Ag_2PO_3F	$C2/c$	291[a]	0.032 @ 546 nm[e]	19
20	$KAg_3(PO_3F)_2$	$P2/c$	256[a]	0.077 @ 546 nm[e]	19
21	$RbAg_3(PO_3F)_2$	$P2/c$	256[a]	0.080 @ 546 nm[e]	19
22	$NH_4Ag_3(PO_3F)_2$	$P3_121$	271[a]	0.101 @ 546 nm[e]	19
23	$KBaSr(PO_2F_2)(PO_3F)_2$	$P2_1/c$	200[a]	0.042 @ 550 nm[e]	20
24	$Na_{1.5}Rb_{0.5}PO_3F·H_2O$	$Pmn2_1$	200[a]	0.040 @ 546 nm[e]	21
25	$(N_2H_6)[HPO_3F]_2$	$C2/m$	200[a]	0.077 @ 1064 nm[d]	22
26	$SnPO_3F$	$P2_1/c$	258[c]	0.075 @ 1064 nm[d]	23
27	$SrPO_3F$	$P2_1/c$	173[c]	0.034 @ 1064 nm[d]	23
28	$(NH_4)_3[Sc_3F_5(PO_4)(PO_3F)_2$	Cc	200[b]	0.010 @ 550 nm[e]	24
29	$(C_3N_6H_7)_2PO_3F·4H_2O$	$P2_1/n$	231[a]	0.38 @ 546 nm[d]	25
30	$SrPO_3F·H_2O$	$P2_1/c$	216[c]	0.037 @ 546 nm[d]	19
31	$LiNH_4PO_3F$	$P2_1/c$	184[c]	0.034 @ 546 nm[d]	19
32	$LiKPO_3F·H_2O$	$P2_1/c$	247[c]	0.017 @ 546 nm[d]	19
33	$CdPO_3F·2H_2O$	$P\bar{1}$	340[c]	0.038 @ 546 nm[d]	19
34	$Mg(NH_4)_2(PO_3F)_2·2H_2O$	$C2/m$	261[c]	0.046 @ 546 nm[d]	19
35	$CaPO_3F·2H_2O$	$P\bar{1}$	241[c]	0.028 @ 546 nm[d]	19
36	$(NH_4)_2PO_3F·H_2O$	$P2_1/c$	251[c]	0.015 @ 546 nm[d]	19
37	$NH_4PO_2F_2$	$Pnma$	152[c]	0.046 @ 1064 nm[d]	15
38	KPO_2F_2	$Pnma$	156[c]	0.047 @ 1064 nm[d]	15
39	$CsPO_2F_2$	$Pnma$	155[c]	0.045 @ 1064 nm[d]	15
40	$[C(NH_2)_3]_2PO_2F_2$	$Pnma$	180[c]	0.091 @ 532 nm[d]	26
41	$K_4(PO_2F_2)_2(S_2O_7)$	$C2/c$	200[a]	0.010 @ 546 nm[e]	27
42	$KLa(PO_2F_2)_4$	$P2_1/c$	180[b]	0.019 @ 546 nm[e]	28
43	$NH_4La(PO_2F_2)_4$	$P2_1/c$	190[a]	0.017 @ 546 nm[e]	28
44	$(NH_4)_2Ba(PO_2F_2)_4$	$P2/n$	180[b]	0.022 @ 1064 nm[d]	29
45	$NH_4Mg(PO_2F_2)_3$	$Cmcm$	222[c]	0.033 @ 546 nm[d]	29
46	$NH_4Sr(PO_2F_2)_3$	$P\bar{1}$	214[c]	0.035 @ 546 nm[d]	29
47	$Ba(PO_2F_2)_2$	$I\bar{4}2d$	214[c]	0.011 @ 546 nm[d]	29

[a]diffuse reflection spectrum, [b]Transmittance spectrum, [c]calculated data from the reported references, [d]calculated birefringence, [e]measured birefringence.

Table S10. Real-space atom-cutting results of calculated birefringence for $(CN_4H_7)_2PO_3F·H_2O$ and $(C_4N_4H_{11})_2PO_3F·H_2O$.

Cut unit	none	$[H_2O]$	$[PO_3F]$	Cations
$(CN_4H_7)_2PO_3F·H_2O$	0.116	0.116	0.100	0.034
$(C_4N_4H_{11})_2PO_3F·H_2O$	0.165	0.165	0.151	0.046

Figure S1. TG-DSC curves of (a) $(CN_4H_7)_2PO_3F·H_2O$ and (b) $(C_4N_4H_{11})_2PO_3F·H_2O$. Experimental powder XRD patterns at different temperatures of (c) $(CN_4H_7)_2PO_3F·H_2O$ and (d) $(C_4N_4H_{11})_2PO_3F·H_2O$.

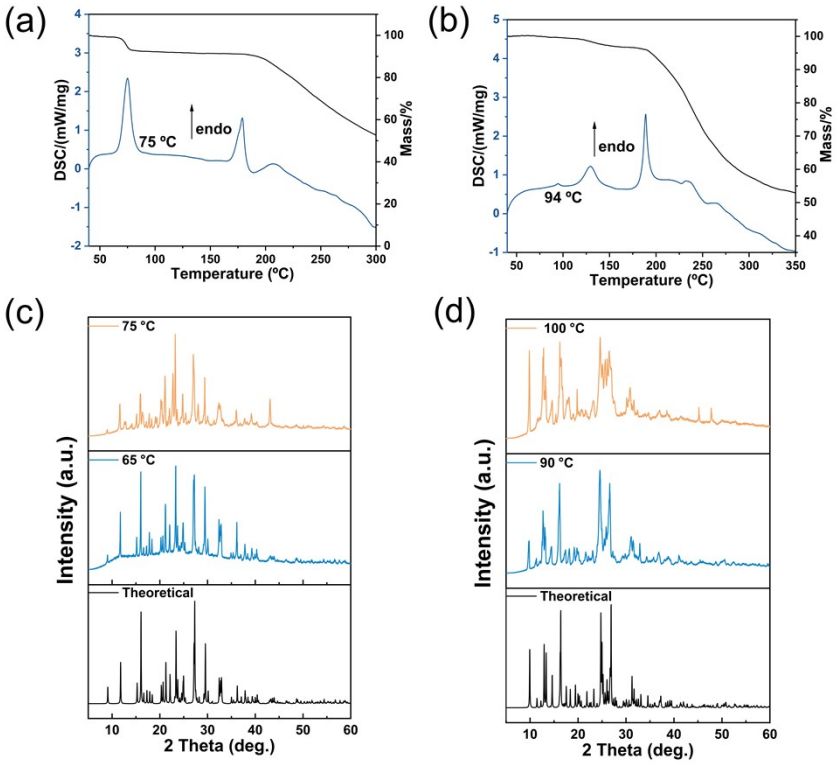


Figure S2. IR spectra of (a) $(CN_4H_7)_2PO_3F{\cdot}H_2O$ and (b) $(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$.

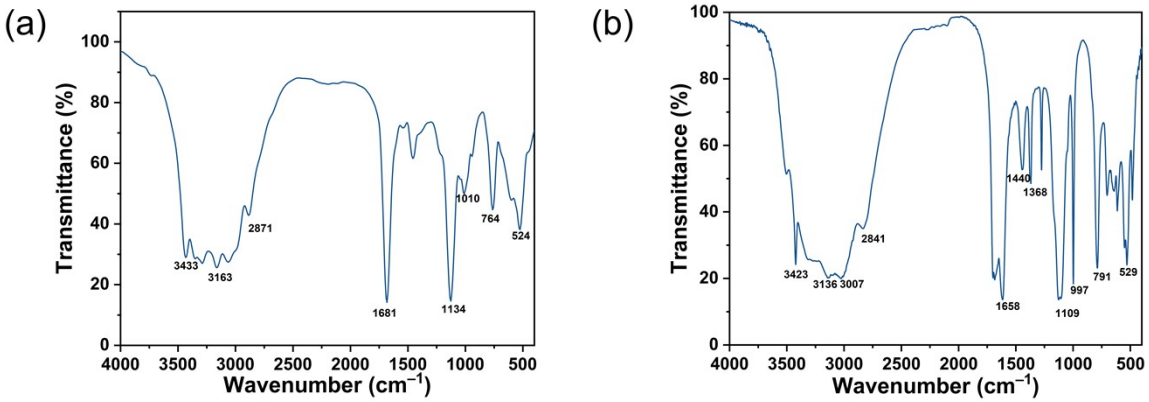
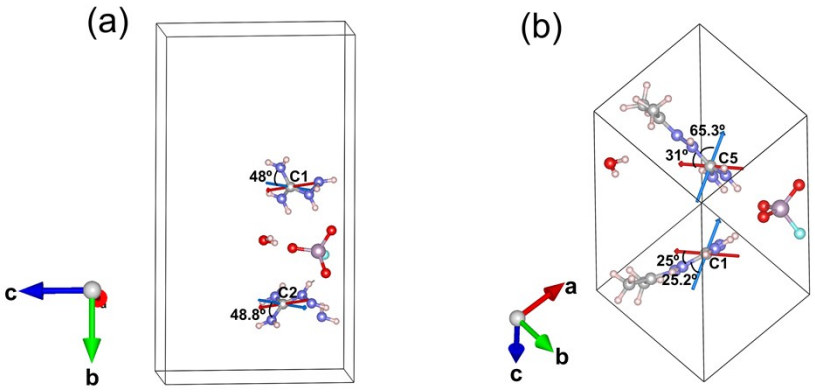


Figure S3. Directions of n_{max} and n_{min} for planar π-conjugated units in (a) $(CN_4H_7)_2PO_3F{\cdot}H_2O$ and (b) $(C_4N_4H_{11})_2PO_3F{\cdot}H_2O$. Red and blue arrows mean the directions of n_{max} and n_{min}, respectively.



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