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Designing promising ultraviolet (UV) birefringent crystals with different hydrogen-bonded phosphate frameworks

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Table S1. Crystallographic data for **I** and **II**.

Compound	**I**	**II**
empirical formula	$C_6H_9N_2O_5P$	$C_6H_8NO_6P$
formula weight	220.12	221.10
crystal system	orthorhombic	orthorhombic
space group	*Fdd*2	*Pbca*
T (K)	299.73(10)	293(2)
a (Å)	35.3496(12)	12.9290(2)
b (Å)	14.3166(5)	7.69510(10)
c (Å)	7.1073(2)	17.0913(3)
V (Å^3)	3596.9(2)	1700.41(5)
Z	16	8
D_c (g/cm^3)	1.626	1.727
μ (mm^{-1})	2.799	3.021
goodness of fit on F^2	1.060	1.162
Flack parameter	0.02(3)	none
R_1, wR_2 [$I>2\sigma(I)$][a]	0.0276, 0.0692	0.0453, 0.1021
R_1, wR_2 (all data)[a]	0.0295, 0.0701	0.0500, 0.1082

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, and $wR_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **I**.

Atom	x	y	z	U(eq)
P1	3487.7(2)	3847.4(4)	2684.9(7)	34.86(18)
O1	5129.3(5)	3810.8(19)	2712(3)	59.5(6)
O2	3588.8(5)	4316.7(16)	4514(3)	44.2(4)
O3	3349.5(6)	4489.4(15)	1175(3)	47.5(5)
O4	3178.4(6)	3079.0(14)	3061(3)	50.2(5)
O5	3828.6(6)	3286.4(17)	1872(3)	48.9(5)
N1	4228.0(6)	4007.1(16)	6178(3)	37.8(5)
N2	5547.4(6)	3538(2)	5037(4)	48.0(6)
C1	5203.0(8)	3699(2)	4395(4)	41.4(6)
C2	4882.6(7)	3757.0(18)	5773(3)	35.7(5)
C3	4529.6(7)	3956.4(18)	5054(4)	37.1(5)
C4	4255.3(8)	3866(2)	8030(4)	41.7(6)
C5	4599.9(9)	3676(2)	8828(4)	47.5(7)
C6	4916.0(7)	3619.2(19)	7698(4)	41.9(6)

Table S3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **II**.

Atom	x	y	z	U(eq)
P1	6318.8(4)	11615.3(7)	4778.4(3)	23.56(18)
O1	6357.7(12)	9660(2)	4812.9(10)	30.2(4)
O2	6323.5(14)	12336(2)	3958.5(10)	33.7(4)
O3	7218.3(14)	12417(3)	5266.0(10)	39.6(5)
O4	5351.0(14)	12281(2)	5234.9(12)	41.0(5)
O5	6379.1(15)	5479(2)	3562.6(11)	38.2(4)
O6	6212.1(16)	4251(2)	2388.0(11)	43.5(5)
N1	6267.2(15)	10337(3)	2629.0(12)	31.0(4)
C1	6280.0(17)	5518(3)	2805.9(14)	28.9(5)
C2	6250.7(16)	7313(3)	2468.5(14)	26.8(5)
C3	6163.5(18)	7547(3)	1666.2(14)	31.2(5)
C4	6133(2)	9203(3)	1358.3(15)	35.6(6)
C5	6187.2(19)	10600(3)	1853.9(15)	34.0(5)
C6	6298.0(17)	8753(3)	2947.2(14)	29.6(5)

Table S4. Bond Lengths for **I**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O2	1.506(2)	N2	C1	1.320(4)
P1	O3	1.495(2)	C1	C2	1.500(4)
P1	O4	1.574(2)	C2	C3	1.378(3)
P1	O5	1.559(2)	C2	C6	1.388(4)
O1	C1	1.235(4)	C4	C5	1.371(4)
N1	C3	1.334(3)	C5	C6	1.378(4)
N1	C4	1.335(4)			

Table S5. Bond Lengths for **II**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O1	1.5065(17)	N1	C6	1.336(3)
P1	O2	1.5070(17)	C1	C2	1.497(3)
P1	O3	1.5581(17)	C2	C3	1.388(3)
P1	O4	1.5611(18)	C2	C6	1.379(3)
O5	C1	1.300(3)	C3	C4	1.379(3)
O6	C1	1.212(3)	C4	C5	1.371(4)
N1	C5	1.344(3)			

Table S6. Bond Angles for **I**.

Atom	Atom	Atom	Angle/	Atom	Atom	Atom	Angle/
O2	P1	O4	109.27(12)	N2	C1	C2	118.7(3)
O2	P1	O5	111.47(12)	C3	C2	C1	116.9(2)
O3	P1	O2	115.00(13)	C3	C2	C6	118.2(2)
O3	P1	O4	108.94(12)	C6	C2	C1	124.9(2)
O3	P1	O5	107.66(12)	N1	C3	C2	120.8(2)
O5	P1	O4	103.88(13)	N1	C4	C5	120.1(3)
C3	N1	C4	121.6(2)	C4	C5	C6	119.4(3)
O1	C1	N2	123.5(3)	C5	C6	C2	119.8(2)
O1	C1	C2	117.8(2)				

Table S7. Bond Angles for **II**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	P1	O2	113.80(10)	O6	C1	C2	120.9(2)
O1	P1	O3	110.47(10)	C3	C2	C1	120.2(2)
O1	P1	O4	109.57(10)	C6	C2	C1	120.8(2)
O2	P1	O3	110.41(10)	C6	C2	C3	119.0(2)
O2	P1	O4	110.32(11)	C4	C3	C2	120.0(2)
O3	P1	O4	101.59(11)	C5	C4	C3	119.2(2)
C6	N1	C5	122.8(2)	N1	C5	C4	119.7(2)
O5	C1	C2	114.0(2)	N1	C6	C2	119.4(2)
O6	C1	O5	125.0(2)				

Table S8. Hydrogen Bonds for **I**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O4	H4A	O1[1]	0.82	1.80	2.621(3)	175.3
O5	H5A	O3[2]	0.82	1.74	2.527(3)	160.7
N1	H1	O2	0.86	1.73	2.589(3)	173.6
N2	H2A	O2[3]	0.86	2.09	2.922(3)	164.3
N2	H2B	O3[4]	0.86	2.08	2.898(3)	157.9

[1] -1/4+X, 3/4-Y, 1/4+Z; [2] 3/4-X, -1/4+Y, 1/4+Z; [3] 1/4+X, 3/4-Y, -1/4+Z; [4] 1/4+X, 3/4-Y, 3/4+Z. Only the hydrogen bonds are selected with max D-A distance 3 Å and minimum angle 120°.

Table S9. Hydrogen Bonds for **II**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O3	H3A	O1[1]	0.82	1.88	2.640(2)	152.7
O4	H4A	O1[2]	0.82	1.86	2.668(2)	168.2
O5	H5	O2[3]	0.86	1.79	2.513(2)	139.7
N1	H1	O2	0.86	1.95	2.745(3)	153.1
C5	H5A	O6[4]	0.93	2.31	2.954(3)	125.7

[1] 3/2-X, 1/2+Y, +Z; [2] 1-X, 2-Y, 1-Z; [3] +X, -1+Y, +Z; [4] +X, 1+Y, +Z. Only the hydrogen bonds are selected with max D-A distance 3 Å and minimum angle 120°.

Table S10. List of π-π interactions for **I**.

Cg(I)-Cg(J)	ARU(J)	Cg-Cg (Å)	Alpha (°)	Beta (°)	Gamma (°)	CgI_Perp (Å)	CgJ_Perp (Å)
Cg(1)-Cg(1)	a	4.5654(15)	15.10(13)	33.1	33.1	3.8223(11)	3.8223(11)

a: 1-X, 1-Y, Z; Cg(I) = Plane number I (= ring number in () above); Alpha = Dihedral Angle between Planes I and J (Deg); Beta = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg); Gamma = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg); Cg-Cg = Distance between ring Centroids (Ang.); CgI_Perp = Perpendicular distance of Cg(I) on ring J (Ang.); CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)

Table S11. List of π-π interactions for **II**.

Cg(I)-Cg(J)	ARU(J)	Cg-Cg (Å)	Alpha (°)	Beta (°)	Gamma (°)	CgI_Perp (Å)	CgJ_Perp (Å)
Cg(1)-Cg(1)	a	5.1088(13)	0.12(11)	50.8	50.7	3.2334(9)	3.2256(9)
Cg(1)-Cg(1)	b	5.0811(13)	9.06(11)	49.3	49.4	3.3044(9)	3.3122(9)

a: 1-X, -1/2+Y, 1/2-Z; b: 3/2-X, -1/2+Y, Z.

Table S12. Theoretical and experimental results of elemental analysis for **I** and **II**.

Weight	**I**		**II**	
(%)	(Exp.)	(Cal.)	(Exp.)	(Cal.)
C	32.54	32.71	30.57	32.43
H	3.98	4.09	3.59	4.05
N	12.43	12.72	6.53	6.31
Ratio				
C	5.97	6	5.61	6
H	8.76	9	7.90	8
N	1.95	2	0.99	1

Table S13. The assignments of the infrared absorption peaks for **I** and **II**.

Assignment (cm^{-1})	**I**	**II**
N-H	3100, 612, 527	3131, 514
O-H	1376	3070, 1336
C=O	1696	1709
C=C	1638, 1554	1632, 1465
P-O	1197, 1083, 958, 527	1198, 1055, 952, 514

Table S14. Birefringence comparison between title compounds and reported phosphates or sulfates containing organic groups

Compounds	Birefringence (Δn)	Ref.[c]
I	0.196 @ 546 nm[a]	This work
II	0.284 @ 546 nm[a]	
$(C_4H_6N_3)^+(H_2PO_3)^-$	0.225 @ 589.3 nm[a]	37
$[(C(NH_2)_3]_3PO_4\cdot 2H_2O$	0.055 @ 546 nm[a]	38
$[C(NH_2)_3]_6(PO_4)\cdot 3H_2O$	0.078 @ 546 nm[a]	39
$[C(NH_2)_3]SbFPO_4\cdot H_2O$	0.151 @ 546 nm[a]	64
$[C(NH_2)_3]_2Sb_3F_3(HPO_3)_4$	0.027 @ 546 nm[a]	64
$NaIn(C_2O_4)(HPO_4)(H_2O)_5$	0.098 @ 546 nm[a]	65
$([Te(C_6H_5)_2][PO_3(OH)]_n$	0.133 @ 550 nm[a]	66
$(C_5H_6ON)^+(H_2PO_4)^-$	0.25 @ 1064 nm[b]	41
$(C_3H_7N_6)_6(H_2PO_4)_4(HPO_4)\cdot 4H_2O$	0.220 @ 1064 nm[b]	40
$(N_2H_6)[HPO_3F]_2$	0.077 @ 1064 nm[b]	67
$[C(NH_2)_3]_2PO_3F$	0.039 @ 532 nm[b]	60
$[C(NH_2)_3]_2HPO_4\cdot H_2O$	0.014 @ 532 nm[b]	59
$[C_5H_6O_2N_3][HSO_4]\cdot H_2O$	0.25 @ 1064 nm[b]	68
$Te(CS(NH_2)_2)_4SO_4\cdot 2H_2O$	0.210 @ 546.1 nm[a]	70
$(C_3H_7N_6)_2SO_4\cdot 2H_2O$	0.173 @ 1064 nm[b]	40
$C(NH_2)_3SO_3F$	0.133 @ 1064 nm[b]	69

a: experimental value; b: theoretical value; c: the references in the table refer to those in the main text.

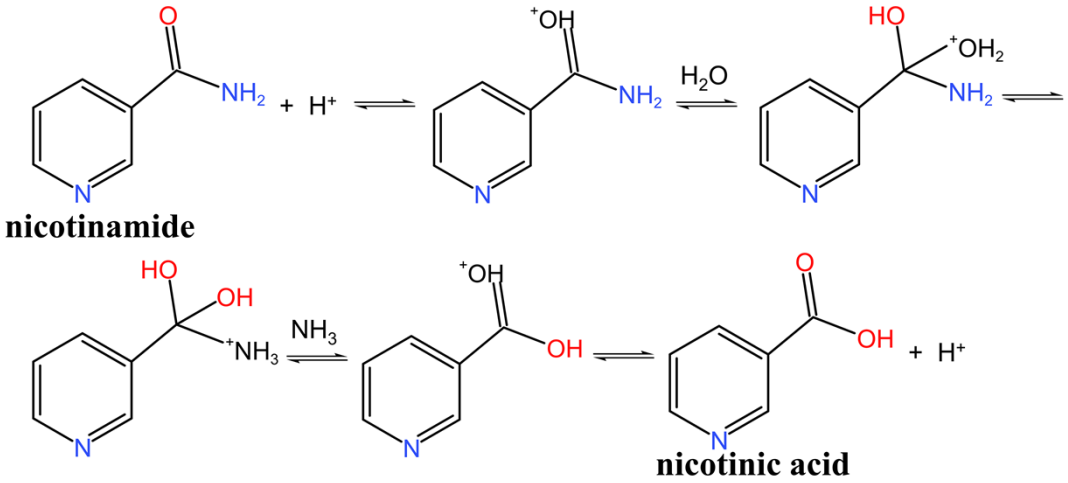

Figure S1. The reaction process from nicotinamide to nicotinic acid in acid solutions.

Figure S2. Simulated and measured powder X-ray diffraction patterns for **I** (a) and **II** (b).

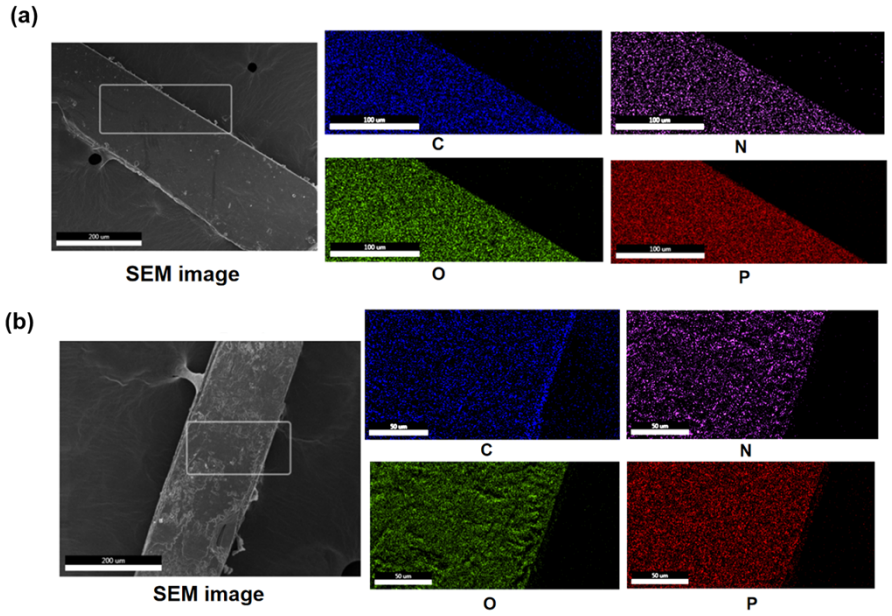

Figure S3. Sem images for **I** (a) and **II** (b).

Figure S4. IR spectra for **I** (a) and **II** (b).

Figure S5. TG and DTA for **I** (a) and **II** (b).

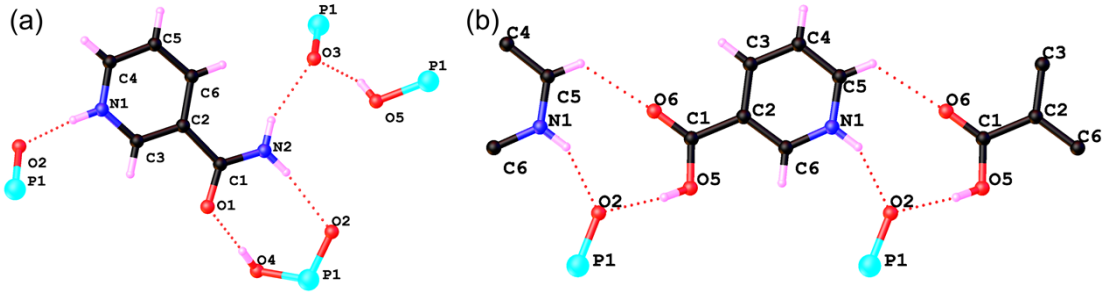

Figure S6. Hydrogen bonds around organic groups for **I** (a) and **II** (b).

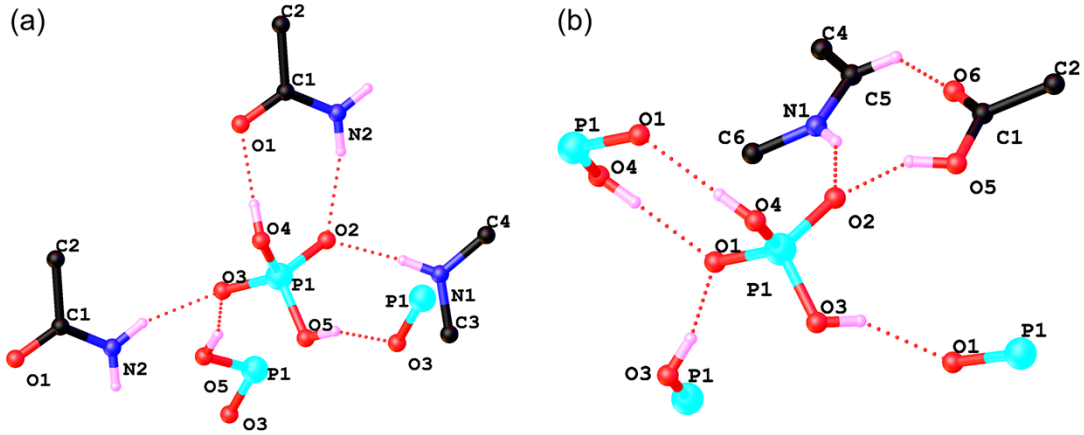

Figure S7. Hydrogen bonds around $H_2PO_4^-$ group for **I** (a) and **II** (b).

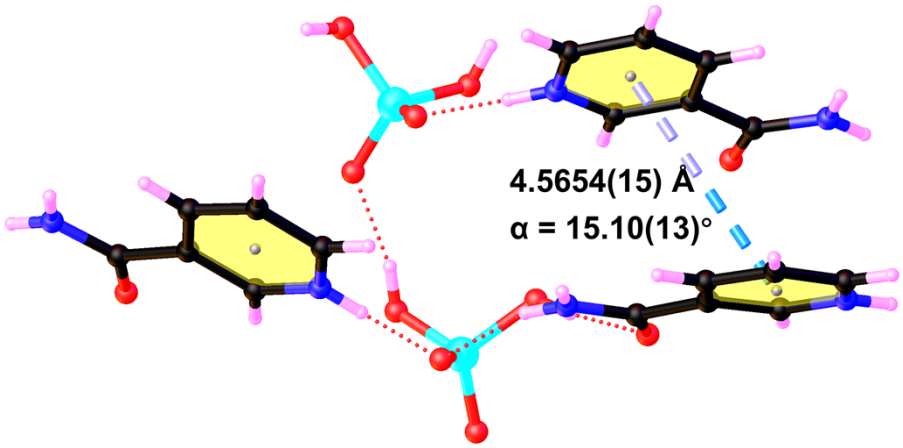

Figure S8. The π-π and dipole-dipole interactions in **I**.

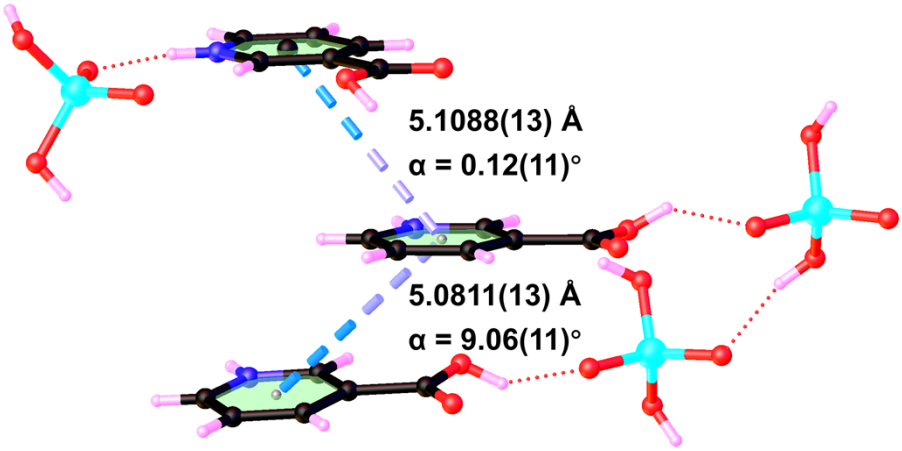

Figure S9. The π-π and dipole-dipole interactions in **II**.

Figure S10. The calculated band structures of **I** (a) and **II** (b).

Figure S11. The thickness of **I** (a) and **II** (b) crystals used for birefringence measurements.

Figure S12. The wavelength-dependent refractive index of **I** (a) and **II** (b).

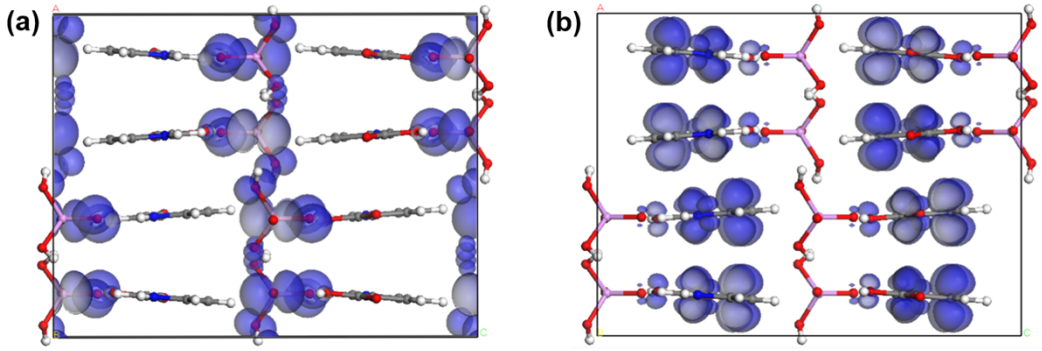

Figure S13. The LUMO and HOMO images of **II**.