Supporting Information

Large Optical Anisotropy in Noncentrosymmetric Phosphate with Pseudo 2D Intercalated Layer

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Table S1. Selected bond distances (Å) and angles (°) for $(C_4H_7N_2)(H_2PO_4)$.

Atom to atom	Length (Å)	Atom to atom	Length (Å)
P(1)-O(1)	1.5339(18)	P(1)-O(2)	1.5653(19)
P(1)-O(3)	1.515(2)	P(1)-O(4)	1.5115(18)
N(1)-C(1)	1.463(3)	N(1)-C(2)	1.321(3)
N(1)-C(4)	1.367(4)	N(2)-C(2)	1.310(3)
N(2)-C(3)	1.358(4)	C(3)-C(4)	1.336(4)
Atom to atom to atom	**Angle (°)**	**Atom to atom to atom**	**Angle (°)**
O(1)-P(1)-O(2)	104.90(11)	O(1)-P(1)-O(3)	111.57(11)
O(1)-P(1)-O(4)	110.49(11)	O(2)-P(1)-O(3)	109.12(12)
O(2)-P(1)-O(4)	109.26(11)	O(3)-P(1)-O(4)	111.28(12)
C(1)-N(1)-C(2)	126.5(2)	C(1)-N(1)-C(4)	125.7(2)
C(2)-N(1)-C(4)	107.8(2)	C(2)-N(2)-C(3)	108.7(2)
N(1)-C(2)-N(2)	109.1(2)	C(4)-C(3)-N(2)	107.1(3)
C(3)-C(4)-N(1)	107.3(2)		

Table S2. Selected bond distances (Å) and angles (°) for $(C_3H_5N_2)(H_2PO_4)$.

Atom to atom	Length (Å)	Atom to atom	Length (Å)
P(1)-O(1)	1.5043(15)	P(1)-O(2)	1.5630(17)
P(1)-O(3)	1.5059(19)	P(1)-O(4)	1.5739(18)
N(1)-C(1)	1.321(3)	N(1)-C(2)	1.369(3)
N(2)-C(1)	1.320(3)	N(2)-C(3)	1.376(3)
C(2)-C(3)	1.344(4)		
Atom to atom to atom	**Angle (°)**	**Atom to atom to atom**	**Angle (°)**
O(1)-P(1)-O(2)	109.42(10)	O(1)-P(1)-O(3)	114.90(10)
O(1)-P(1)-O(4)	106.69(9)	O(2)-P(1)-O(3)	107.19(10)
O(2)-P(1)-O(4)	107.35(10)	O(3)-P(1)-O(4)	111.05(11)
C(1)-N(1)-C(2)	108.4(2)	C(1)-N(2)-C(3)	108.4(2)
N(1)-C(1)-N(2)	109.0(2)	N(1)-C(2)-C(3)	107.3(2)
N(2)-C(3)-N(2)	106.8(2)		

Table S3. Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $(C_4H_7N_2)(H_2PO_4)$ and $(C_3H_5N_2)(H_2PO_4)$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

$(C_4H_7N_2)(H_2PO_4)$				
Atom	x	y	z	$U_{(eq)}$ (Å^2)
P(1)	2544.2(8)	5214.6(7)	364.8(7)	39.9(2)
O(1)	3885(2)	6136(2)	1053(2)	53.4(5)
O(2)	1546(2)	6120(2)	−725(2)	58.4(6)
O(3)	3275(2)	4047(2)	−355(2)	58.3(6)
O(4)	1419(2)	4734(2)	1396.7(17)	52.1(5)
C(1)	4369(4)	6960(3)	6907(3)	57.7(8)
C(2)	3168(4)	6271(3)	4584(3)	49.6(7)
C(3)	2163(4)	4322(3)	5021(3)	59.9(8)
C(4)	2871(4)	4825(3)	6197(3)	59.9(8)
N(1)	3499(3)	6053(2)	5911(2)	44.5(5)
N(2)	2361(3)	5241(2)	4028(2)	49.1(6)
$(C_3H_5N_2)(H_2PO_4)$				
Atom	x	y	z	$U_{(eq)}$ (Å^2)
P(1)	6728.3(6)	5772.1(3)	7181.4(14)	25.11(16)
O(1)	7530(2)	6532.4(8)	6778(4)	35.5(4)
O(2)	7669(2)	5304.8(9)	9463(4)	32.9(4)
O(3)	6635(2)	5286.9(10)	4556(4)	38.2(4)
O(4)	5000(2)	5936.4(9)	8408(4)	35.5(4)
C(1)	5351(3)	7570.4(14)	1587(5)	33.9(6)
C(2)	5861(3)	8787.1(14)	1852(7)	39.9(6)
C(3)	6782(3)	8432.8(14)	3787(6)	39.8(6)
N(1)	4980(2)	8239.6(11)	490(5)	33.9(5)
N(2)	6441(2)	7668.2(12)	3591(5)	36.4(5)

Table S4. Hydrogen-bonding interactions for $(C_4H_7N_2)(H_2PO_4)$ and $(C_3H_5N_2)(H_2PO_4)$.

$(C_4H_7N_2)(H_2PO_4)$				
D-H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(2)-H(2)···O(4)	1.05	1.44	2.491(2)	175
O(1)-H(1)···O(3)	0.86	1.81	2.668(3)	171
O(2)-H(2B)···O(4)	0.82	1.78	2.591(2)	169
C(3)-H(3)···O(1)	0.93	2.56	3.428(4)	157
C(4)-H(4)···O(3)	0.93	2.56	3.455(4)	162
$(C_3H_5N_2)(H_2PO_4)$				
D-H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(1)-H(1)···O(1)	0.86	1.86	2.714(3)	169
N(2)-H(2)···O(1)	0.86	1.80	2.657(3)	174
O(2)-H(2B)···O(3)	0.82	1.75	2.553(3)	166
O(4)-H(4)···O(3)	0.82	1.79	2.599(2)	169
C(1)-H(1A)···O(4)	0.93	2.40	3.252(3)	152
C(2)-H(2A)···O(2)	0.93	2.56	3.180(3)	124

Table S5. π-π stacking interactions in $(C_4H_7N_2)(H_2PO_4)$ and $(C_3H_5N_2)(H_2PO_4)$.

$(C_4H_7N_2)(H_2PO_4)$						
Number	*Cg*(I)–>*Cg*(J)	*D*	*η*	*d*	*ϑ*	Strong or Weak
1	*Cg*(1)–>*Cg*(1)	4.627	0	3.704	36.82	weak
2	*Cg*(1)–>*Cg*(1)	3.679	0	3.537	15.98	strong
$(C_3H_5N_2)(H_2PO_4)$						
Number	*Cg*(I)–>*Cg*(J)	*D*	*η*	*d*	*ϑ*	Strong or Weak
1	*Cg*(1)–>*Cg*(1)	4.720	0	3.197	47.38	weak
2	*Cg*(1)–>*Cg*(1)	4.720	0	3.197	47.38	weak
3	*Cg*(1)–>*Cg*(1)	4.720	12.08	2.786	53.82	weak
4	*Cg*(1)–>*Cg*(1)	4.720	12.08	3.259	46.33	weak

Note: 1. *Cg*(I) represents the center of mass(I) of the five-membered ring imidazole plane, and the coordinates of *Cg*(1) are (0.28, 0.53, 0.51) and (0.59, 0.81, 0.23) in $(C_4H_7N_2)(H_2PO_4)$ and $(C_3H_5N_2)(H_2PO_4)$, respectively; 2. *D*: the distance between the centroids of the rings (Å); 3. *η*:the dihedral angle (°) between plane I and J; 4. *d*: vertical distance between adjacent imidazole planes (Å); 5. *ϑ*: displacement angle, the angle between the connection of adjacent centroids and the vertical line formed by the corresponding plane (°).

Table S6. Optical properties for selected phase-matching UV NLO phosphates.

Compound	Space Group	Δ*n* at 1064 nm	Reference
KH_2PO_4 (KDP)	$I\bar{4}2d$	0.034[b]	36
$KTiOPO_4$ (KTP)	$Pna2_1$	0.0921[b]	35
LAP	$P2_1$	0.075[b]	87
$Ba_3P_3O_{10}Cl$	$Pca2_1$	0.028[a]	16
$Ba_3P_3O_{10}Br$	$P2_12_12_1$	0.023[a]	16
$RbMgPO_4{\cdot}6H_2O$	$Pmn2_1$	0.005[a]	17
$CsMgPO_4{\cdot}6H_2O$	$P6_3/mmc$	0.006[a]	17
$NH_4MgPO_4{\cdot}6H_2O$	$Pmn2_1$	0.0063[a]	18
$KMgPO_4{\cdot}6H_2O$	$Pmn2_1$	0.01[a]	18
$LiCs_2PO_4$	$Cmc2_1$	0.01[a]	85
$RbNaMgP_2O_7$ (LTP)	$Pna2_1$	0.031 at 532 nm[a]	21
$RbNaMgP_2O_7$ (HTP)	$Ccm2_1$	0.035 at 532 nm[a]	21
$NaNH_4PO_3F{\cdot}H_2O$	Pc	0.053 at 589.3 nm[b]	84
$RbTiOPO_4$	$Pna2_1$	0.0884[b]	36
$Na_3TaP_2O_9$	$P2_12_12_1$	0.1101 (static)[a]	37
$K_2ZnMoP_2O_{10}$	$P2_12_12_1$	0.0534 at 450.2 nm[b]	38
$Na_{12}(NbO)_3(PO_4)_7$	$Pna2_1$	0.03 (static)[a]	39
$Rb_3PbBi(P_2O_7)_2$	$P2_12_12_1$	0.031[b]	40
$Cs_3PbBi(P_2O_7)_2$	$P2_12_12_1$	0.02[b]	40
$Rb_3BaBi(P_2O_7)_2$	$P2_1$	0.025[a]	41
$Cs_3BaBi(P_2O_7)_2$	$P2_12_12_1$	0.025[a]	41
$K_2Sb(P_2O_7)F$	$P4bm$	0.157 at 546 nm[b]	42
$Rb_2Sb(P_2O_7)F$	$P4bm$	0.15 at 546 nm[b]	43
Sn_2PO_4Cl	$Pna2_1$	0.162 at 546 nm[b]	44
β-$Cd(PO_3)_2$	$P2_12_12_1$	0.059[a]	1
$(NH_4)_3(H_3O)Zn_4(PO_4)_4$	$P6_3$	0.032[a]	45
$LiHgPO_4$	$P\bar{4}2_1m$	0.068[b]	46
$[C(NH_2)_3]_6(PO_4)_2{\cdot}3H_2O$	Cc	0.078 at 546 nm[b]	55
4HPP	$P2_12_12_1$	0.25[a]	50
2APP	$P2_1$	0.225[b]	51
$[C(NH_2)_3]_2PO_3F$	Cm	0.039 at 532 nm[a]	52
$[C(NH_2)_3]_3PO_4{\cdot}2H_2O$	$Pna2_1$	0.055 at 546 nm[b]	49
$(C_3H_7N_6)_6(H_2PO_4)_4(HPO_4){\cdot}4H_2O$	$P2_1$	0.220[a]	53
$(C_3H_5N_2)(H_2PO_4)$	$Pna2_1$	0.15 at 546 nm[b]	this work

Notes:

[a] Cal. Birefringence

[b] Exp. Birefringence

LAP: $(H_2N)_2CNH(CH_2)_3CH(NH_3)COO{\cdot}H_2PO_4{\cdot}H_2O$

4HPP: $(C_5H_6ON)(H_2PO_4)$

2APP: $(C_4H_6N_3)(H_2PO_3)$

Table S7. The linear and nonlinear optical properties of $(C_3H_5N_2)(H_2PO_4)$ were calculated by real-space atom cutting method.

		Total	$[C_3H_5N_2]^+$	$[H_2PO_4]^-$
$(C_3H_5N_2)(H_2PO_4)$	n_x	1.51	1.42	1.22
	n_y	1.578	1.46	1.22
	n_z	1.50	1.40	1.20
	Δn @ 546 nm	0.078	0.057 (78.08%)[a]	0.016 (21.92%)
	d_{15}	−0.045	0.034	−0.053
	d_{24}	0.19	0.11	0.25
	d_{33}	−0.49	−0.35 (55.56%)[b]	−0.28 (44.44%)

Notes:

d values in pm/V.

[a]The percentage in the table represents the contribution of each component to Δn.

[b]The percentage in the table represents the contribution of each component to d_{33}.

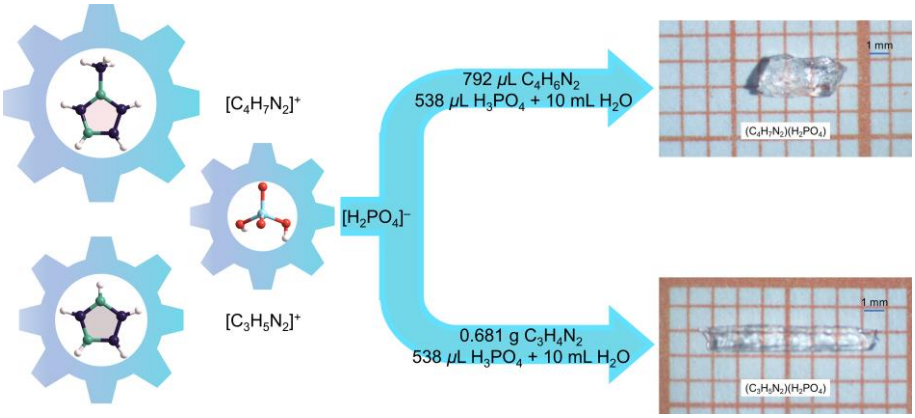

Figure S1. Unpolished photos of $(C_4H_7N_2)(H_2PO_4)$ crystal (top) and $(C_3H_5N_2)(H_2PO_4)$ crystal (bottom).

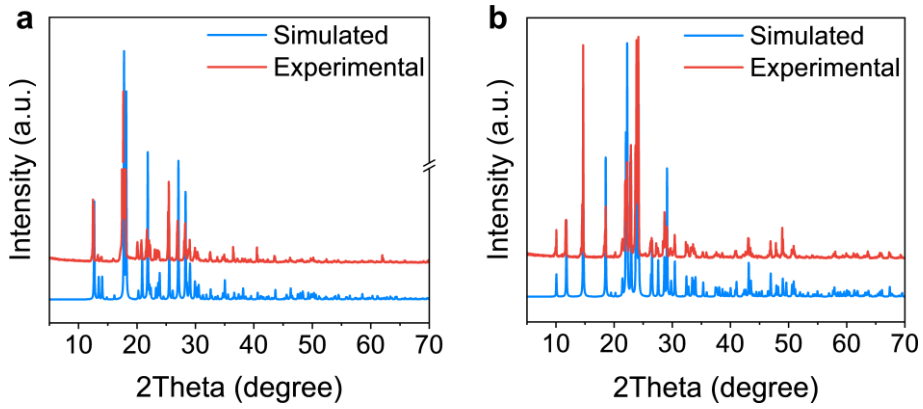

Figure S2. Simulated and experimental powder X-ray diffraction patterns of $(C_4H_7N_2)(H_2PO_4)$ (a) and $(C_3H_5N_2)(H_2PO_4)$ (b).

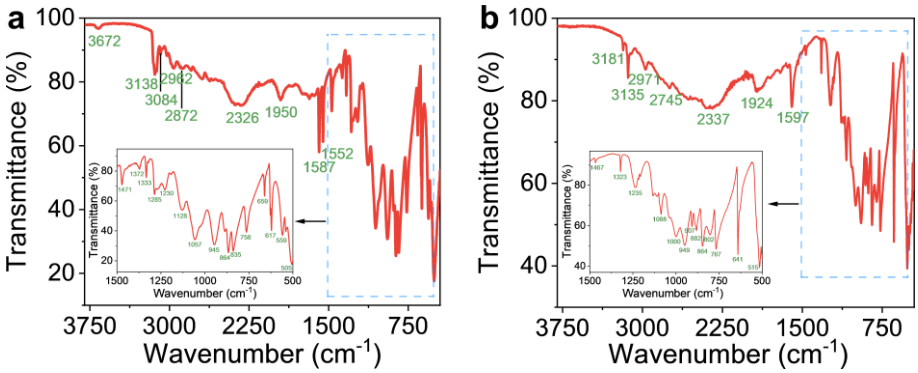

Figure S3. IR spectra of $(C_4H_7N_2)(H_2PO_4)$ (a) and $(C_3H_5N_2)(H_2PO_4)$ (b).

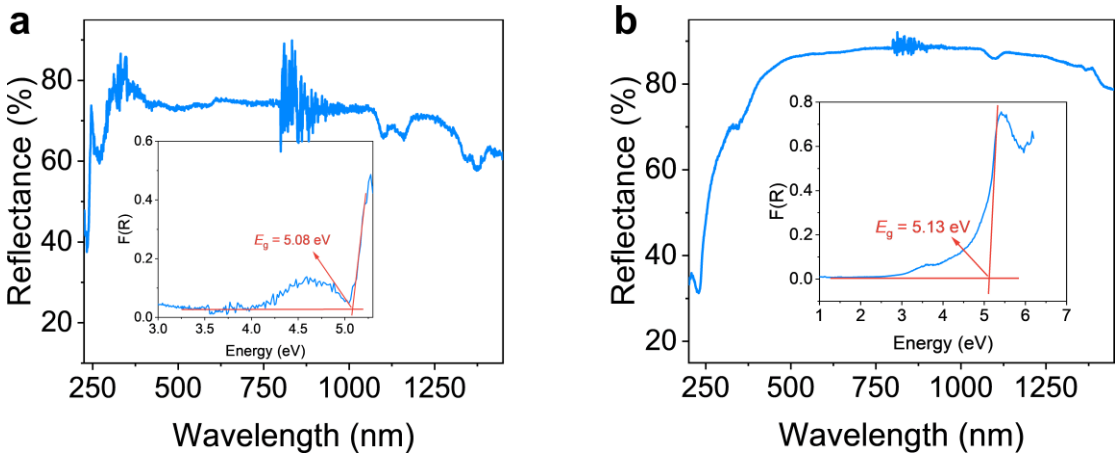

Figure S4. UV-Vis-NIR diffuse reflectance spectra of compound $(C_4H_7N_2)(H_2PO_4)$ (a) and $(C_3H_5N_2)(H_2PO_4)$ (b). The experimental optical band gaps are calculated by the Kubelka-Munk formula, $F(R) = (1 - R)^2/(2R)$, where R is the reflectance.

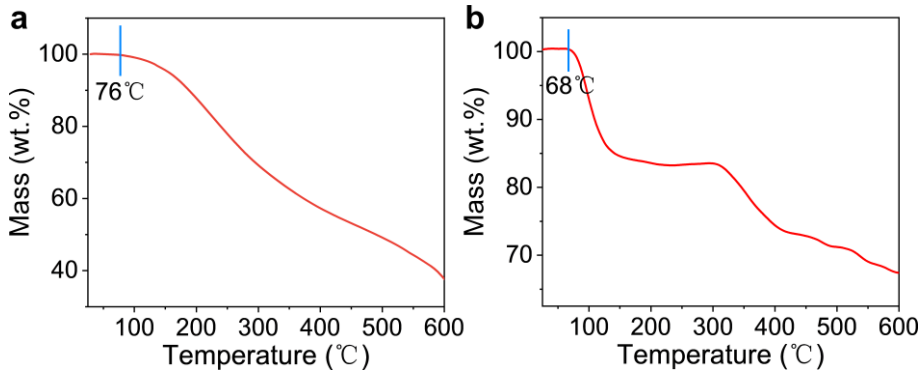

Figure S5. Thermogravimetry (TG) curve of $(C_4H_7N_2)(H_2PO_4)$ (a) and $(C_3H_5N_2)(H_2PO_4)$ (b) under a N_2 atmosphere.

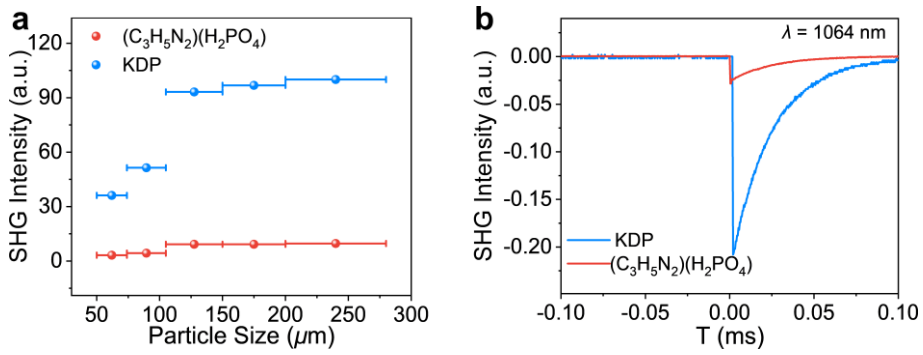

Figure S6. (a) Phase-matching curves of $(C_3H_5N_2)(H_2PO_4)$ with 1064 nm laser radiation. (b) Oscilloscope traces of the SHG signals for powders of $(C_3H_5N_2)(H_2PO_4)$ (105−150 μm) with 1064 nm laser radiation.

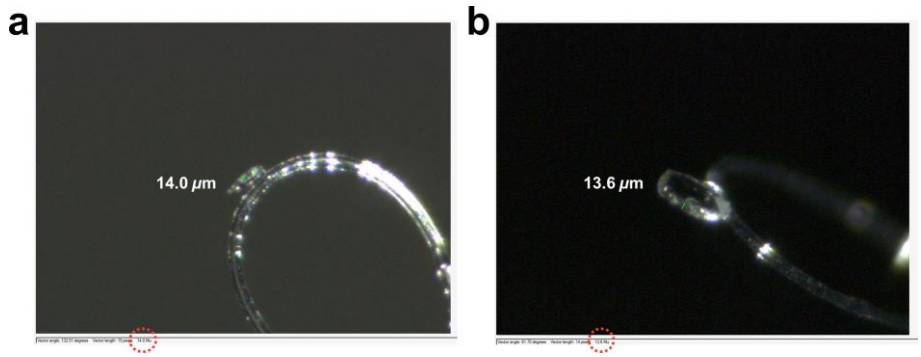

Figure S7. Photograph of the crystal size of $(C_4H_7N_2)(H_2PO_4)$ (a) and $(C_3H_5N_2)(H_2PO_4)$ (b).