Supporting Information

Two mixed P-O anionic phosphates with distinctive structural transformation and deep ultraviolet cutoff edge

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Section S1.

Experimental Section

Reagents. Na_2CO_3 (99.9 %), MgO (99.9 %), CdO (99 %), and $NH_4H_2PO_4$ (99.0 %) were purchased from commercial sources Aladdin and used without further purification.

Synthesis. Polycrystalline powder samples of NMPP and NCPP. were synthesized via conventional high-temperature solid-state reaction. The reagents of the two compounds were initially mixed in stoichiometric proportions and thoroughly ground using an agate mortar. Then the mixtures were put into a muffle furnace and preheated to 350℃ at the rate of 25 ℃/ h, holding for 12 hours at the point to remove CO_2, NH_3 and H_2O. Subsequently, the temperature for NMPP and NCPP was gradually increased to 700 ℃ and 600 ℃ for 36 hours, respectively. Finally, pure polycrystalline samples of the target compounds were successfully obtained. The purity of the samples was confirmed by a Bruker D2 PHASER X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) at room temperature, over a 2ϑ range of 10-70° with a scan step size of 0.02° and a fixed counting time of 1 s per step.

Crystal Growth. Single crystals of NMPP and NCPP were spontaneously grown using the high-temperature solution method with the same procedure. The raw reagents (Na_2CO_3, MgO, $NH_4H_2PO_4$ with a ratio of 2: 3: 4 for NMPP and Na_2CO_3, CdO, $NH_4H_2PO_4$ with a ratio of 2: 3: 5 for NCPP, respectively) were ground homogeneously and then placed into platinum crucibles. The samples were then heated to 880 ℃ in a vertical furnace and maintained at this temperature for 24 hours to ensure complete melting. Subsequently, the temperature was gradually reduced to 650 ℃ at a rate of 2 ℃/h, then to 500 ℃ at a rate of 5 ℃/h. Finally, the samples were rapidly cooled to room temperature, yielding colorless and transparent single crystals.

Single-Crystal X-ray Diffraction. The crystals were determined using single-crystal X-ray diffraction (SC-XRD). The data were collected using a Bruker D8 Quest X diffractometer with graphitic monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The SAINT program was used for diffraction data collection and integration.[1] The OLEX2 system was used to solve and refine the crystal structures, and all atomic positions were refined by a full matrix least squares technique, and at last we used PLATON to check the missing symmetry elements.[2, 3] The detailed crystal data, final atomic coordinates, equivalent

isotropic displacement parameters, bond valencies, selected bond lengths and angles are summarized in Tables S1-S5.

Thermal Behavior Analysis. To check the thermal properties of the compounds, thermogravimetric (TG) and differential thermal analysis (DTA) coupling were performed on a HITACHI STA 7300 thermal analysis instrument. The samples were placed in Al_2O_3 crucibles and heated from 30 ℃ to 1000 ℃, and then cooled to 200 ℃ at a rate of 10 ℃/min in flowing argon atmosphere.

Spectroscopy Analysis. The samples were mixed with KBr in the ratio of 1:100, respectively and was tested by a Shimadzu IR Affinity-1 FTIR spectrometer in the range of 400-4000 cm^{-1}. Diffuse reflectance spectra were tested by Shimadzu SolidSpec-3700DUV in the range of 190-2600 nm. The conversion equation used between reflection and absorption spectra is Kubelka-Munk equation: $F(R) = (1-R)^2/2R = K/S$, where R is reflectance, K is absorption coefficient, and S is scattering coefficient.[4]

Energy Dispersive X-ray Spectroscopy (EDS). Elemental analysis was performed using a LEO-1430VP scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS).

SHG Measurements. Since NMPP has a NCS structure, its SHG property should be investigated. The polycrystalline SHG of NMPP was performed using the Kurtz-Perry method.[5] Since the SHG intensity depends on the particle sizes, polycrystalline samples were ground and sieved into six different particle size ranges: 25-45, 45-62, 62-75, 75-109, 109-150, and 150-212 μm. The measurements were performed with a Q-switched Nd:YAG laser at 1064 nm incident light and the SHG signal was recorded by a photomultiplier tube. For a relevant comparison with known SHG material, commercial NLO crystal KDP was also ground and sieved into the same particle sizes range as reference.

Theoretical Calculations. Since NCPP intrinsically possesses structural disorder at several positions, we just investigated the electronic structure of NMPP. The density function theory (DFT) calculations for NMPP were performed by the CASTEP package.[6] The exchange-correlation effect is implemented by generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function. To achieve energy convergence, the cutoff energy was set as 830 eV and Monkhorst-Pack *k*-point lattice with Brillouin zone densities of 1 × 2 × 4 was used. The refractive index and birefringence were further calculated

by the OptaDOS code.[7, 8] For other calculation parameters and convergence criteria, we used the default values of the CASTEP code. The SHG tensors are further calculated using the "sum over states" (SOS) expressions. Employing scissor corrections, reliable SHG coefficients can be obtained from the GGA calculations. The effective SHG effect of NMPP was measured using a Q-switched 1064 nm Nd: YAG laser by using the improved Kurtz and Perry methods [9, 10].

Table S1. Crystallographic data and structural refinements for NMPP and NCPP.

Empirical formula	NMPP	NCPP
Formula weight	1057.54	961.42
Temperature/ K	296(2)	296(2)
Wavelength/ Å	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	$Pna2_1$	**PError!**
a (Å)	17.9576(12)	6.7307(3)
b (Å)	10.4987(7)	9.6642(5)
c (Å)	6.5119(4)	11.5063(6)
α(°)		98.27
β(°)	90	92.13
γ(°)		90.62
V(Å), *Z*	1227.70(14), 2	740.04(6), 2
Completeness	99.8 %	99.4 %
Density(calculated) [Mg/m^3]	2.861	4.315
Absorption coefficient/ (mm^{-1})	1.006	6.406
F(000)	1040	888
Theta range for data collection/°	4.494 to 55.924	4.26 to 50.1
Limiting indices	-22 ≤ h ≤ 22, -12 ≤ k ≤ 13, -8 ≤ l ≤ 8	-7 ≤ h ≤ 8,-11 ≤ k ≤ 11, -13≤ l≤13
Reflections collected / unique	11176/2638[R(int)=0.0605]	14860/2599[R(int)= 0.0531]
Refinement method	Full-matrix least-squares on F^2	
GOF (F^2)	1.039	1.072
R indices ($I > 2\sigma(I)$)	R_1 = 0.0360, wR_2 = 0.0668	R_1 = 0.0309, wR_2 = 0.0492
R indices (all data)	R_1 = 0.0483, wR_2 = 0.0716	R_1 = 0.0439, wR_2 = 0.0536
Largest diff. peak and hole ($eÅ^{-3}$)	0.46/-0.44	0.89/-0.82

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

Table S2. Atomic coordinates, displacement parameters and BVSs of NMPP.

Atom	x/*a*	y/*b*	z/*c*	U_{eq}[a]	S.O.F	BVS
P1	4308.9(7)	2641.2(13)	3191(2)	8.5(3)	1	4.85
P2	2919.2(7)	5030.8(13)	9624(2)	7.5(3)	1	4.83
P3	3199.4(7)	-120.4(13)	9521(2)	7.9(3)	1	4.80
P4	5512.6(7)	2705.6(13)	99(2)	9.9(3)	1	4.82
Mg1	3607.4(9)	-61.5(16)	4591(3)	9.7(4)	1	1.99
Mg2	3339.2(9)	5054.3(16)	4692(3)	9.5(4)	1	2.03
Mg3	2595.1(10)	2442.7(17)	11909(3)	11.3(4)	1	1.98
Na1	3923.1(12)	2629(2)	-2113(4)	18.2(5)	1	1.00
Na2	4925.5(13)	-257(2)	1772(4)	18.1(6)	1	1.24
Na3	4609.7(12)	5410(2)	10339(4)	22.8(6)	1	0.97
Na4	2934.7(13)	7482.9(19)	12110(4)	18.6(6)	1	1.09
O1	5128(2)	2986(3)	2327(6)	12.7(9)	1	2.03
O2	3762(2)	2587(3)	1450(6)	13.2(9)	1	1.87
O3	4159.7(19)	3729(3)	4655(6)	13.0(8)	1	2.04
O4	4387.1(19)	1387(3)	4319(6)	13.9(9)	1	2.04
O5	5089(2)	3508(3)	-1404(6)	16.8(9)	1	1.97
O6	6315.4(19)	3114(3)	338(6)	13.9(9)	1	1.86
O7	5452.7(18)	1289(3)	-274(6)	12.1(8)	1	2.10
O8	3721(2)	119(3)	7723(6)	12.1(9)	1	1.87
O9	2639.8(19)	-1229(3)	9165(6)	11.3(9)	1	1.92
O10	3636(2)	-432(3)	11472(6)	10.6(9)	1	1.96
O11	2680.8(18)	1043(3)	9775(6)	10.2(8)	1	2.03
O12	2392.9(18)	3874(3)	9914(6)	9.5(8)	1	2.07
O13	2366.0(18)	6143(3)	9233(6)	11.4(9)	1	1.94
O14	3382(2)	5356(3)	11519(6)	10.8(9)	1	2.00
O15	3422(2)	4769(3)	7816(6)	14.3(9)	1	1.92

Table S3. Atomic coordinates, displacement parameters and BVSs of NCPP.

Atom	x/*a*	y/*b*	z/*c*	U_{eq}[a]	S.O.F	BVS
Cd1	8301.4(9)	4099.2(6)	-1173.5(5)	13.19(17)	0.85	2.22
Cd2	1517.1(10)	2221.0(7)	711.6(6)	15.98(18)	0.75	2.30
Cd3	5034.4(12)	720.8(8)	8723.7(7)	18.8(2)	0.6	1.80
Cd4	7341.7(7)	3723.6(5)	3869.5(4)	13.93(16)	1	2.10
Cd5	157.6(9)	2782.4(6)	5937.6(5)	12.10(17)	0.8	2.03
P1	6734(3)	5676.7(18)	1595.2(15)	10.2(4)	1	4.78
P2	6697(3)	2616.5(18)	1062.5(15)	10.2(4)	1	4.85
P3	2264(3)	4246.7(18)	3528.7(15)	9.9(4)	1	4.85
P4	2598(3)	-113.9(18)	6049.1(15)	9.9(4)	1	4.82
P5	-102(3)	716.2(18)	8008.0(15)	9.9(4)	1	4.79
Na1	157.6(9)	2782.4(6)	5937.6(5)	12.10(17)	0.2	1.33
Na2	1517.1(10)	2221.0(7)	711.6(6)	15.98(18)	0.25	1.30
Na3	5034.4(12)	720.8(8)	8723.7(7)	18.8(2)	0.4	1.35
Na4	4636(5)	7583(3)	3699(3)	32.4(8)	1	1.05
Na5	8301.4(9)	4099.2(6)	-1173.5(5)	13.19(17)	0.15	1.32
Na6	2848(4)	1261(2)	3550(2)	8.0(6)	1	1.31
O1	8247(7)	5830(5)	673(4)	13.4(11)	1	1.85
O2	8250(7)	2596(5)	139(4)	14.7(11)	1	1.96
O3	5721(7)	4158(4)	1212(4)	12.7(11)	1	1.94
O4	4944(7)	1646(5)	627(4)	16.9(11)	1	2.04
O5	7640(7)	5697(5)	2831(4)	14.0(11)	1	1.84
O6	5014(7)	6668(5)	1596(4)	13.2(11)	1	1.87
O7	4139(7)	3474(5)	3793(5)	20.0(12)	1	2.03
O8	1745(7)	4106(5)	2200(4)	17.3(11)	1	1.88
O9	2500(7)	5806(4)	4026(4)	14.1(11)	1	2.07
O10	610(7)	3592(5)	4164(4)	12.7(10)	1	2.02
O11	2337(7)	1153(5)	5425(4)	16.5(11)	1	2.19
O12	-965(7)	2021(5)	7605(4)	14.7(11)	1	1.92
O13	662(6)	-181(4)	6822(4)	11.3(10)	1	2.08
O14	-1760(7)	-228(5)	8343(4)	13.5(11)	1	1.98
O15	1611(7)	959(5)	8884(4)	14.9(11)	1	1.96
O16	4464(7)	104(5)	6830(4)	14.9(11)	1	2.13
O17	2544(7)	-1482(4)	5225(4)	13.0(11)	1	1.90
O18	7595(7)	2357(5)	2206(4)	19.0(12)	1	1.87

Table S4. Selected bond distances of NMPP and NCPP.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
		NMPP			
P1	O4	1.514(4)	Na4	O13	2.556(4)
P1	O3	1.512(4)	Na4	$O9^{15}$	2.406(4)
P1	O1	1.616(4)	Na3	O14	2.336(4)
P1	O2	1.502(4)	Na3	O15	2.775(5)
P2	O14	1.526(4)	Na3	$O3^{9}$	2.429(4)
P2	O12	1.550(3)	Na3	$O1^{3}$	3.003(4)
P2	O15	1.509(4)	Na3	$O1^{9}$	2.628(4)
P2	O13	1.554(4)	Na3	$O5^{3}$	2.453(4)
P4	O6	1.512(4)	Na3	$O5^{17}$	2.466(4)
P4	O7	1.511(3)	Na1	$O15^{1}$	2.420(4)
P4	O1	1.634(4)	Na1	$O4^{1}$	2.792(5)
P4	O5	1.498(4)	Na1	$O3^{1}$	2.438(5)
P3	O11	1.545(3)	Na1	$O8^{1}$	2.662(4)
P3	O10	1.528(4)	Na1	O2	2.338(4)
P3	O8	1.520(4)	Na1	O5	2.335(4)
P3	O9	1.556(4)	O14	$Mg2^{3}$	2.091(4)
Mg2	$O14^{1}$	2.091(4)	O12	$Mg1^{4}$	2.126(4)
Mg2	$O11^{10}$	2.106(4)	O12	$Na4^{11}$	2.411(4)
Mg2	O15	2.062(5)	O11	$Mg2^{7}$	2.106(4)
Mg2	O3	2.026(4)	O11	$Na4^{11}$	2.553(4)
Mg2	$O6^{9}$	2.064(4)	O15	$Na1^{3}$	2.420(4)
Mg2	$O9^{10}$	2.242(4)	O10	$Mg1^{3}$	2.069(4)
Mg1	$O12^{11}$	2.126(4)	O10	$Na2^{3}$	2.332(4)
Mg1	$O10^{1}$	2.069(4)	O10	$Na4^{8}$	2.560(4)
Mg1	O4	2.075(4)	O4	$Na2^{12}$	2.342(4)
Mg1	$O7^{12}$	2.125(4)	O4	$Na1^{3}$	2.792(4)
Mg1	O8	2.058(5)	O3	$Na3^{2}$	2.429(4)
Mg1	$O13^{11}$	2.170(4)	O3	$Na1^{3}$	2.438(5)
Mg3	O12	2.020(4)	O6	$Mg2^{2}$	2.064(4)
Mg3	O11	2.029(4)	O6	$Mg3^{19}$	2.583(4)
Mg3	$O6^{14}$	2.583(4)	O6	$Na4^{6}$	2.574(4)
Mg3	$O2^{3}$	2.122(4)	O7	$Mg1^{5}$	2.125(4)
Mg3	$O13^{7}$	2.039(4)	O7	$Na2^{5}$	2.310(5)
Mg3	$O9^{4}$	2.068(4)	O1	$Na3^{2}$	2.628(4)
Na2	$O10^{1}$	2.332(4)	O1	$Na3^{1}$	3.003(4)
Na2	$O4^{5}$	2.342(4)	O8	$Na2^{12}$	2.513(5)

Na2	O4	2.582(4)	O8	Na1[3]	2.662(4)
Na2	O7	2.303(4)	O2	Mg3[1]	2.122(4)
Na2	O7[12]	2.310(5)	O13	Mg1[4]	2.170(4)
Na2	O8[5]	2.513(5)	O13	Mg3[10]	2.039(4)
Na4	O14	2.404(4)	O9	Mg2[7]	2.241(4)
Na4	O12[4]	2.411(4)	O9	Mg3[11]	2.068(4)
Na4	O11[4]	2.553(4)	O9	Na4[8]	2.406(4)
Na4	O10[15]	2.560(4)	O5	Na3[6]	2.466(4)
Na4	O6[17]	2.574(4)	O5	Na3[1]	2.453(4)
			NCPP		
Cd1	O1	2.510(4)	O2	Na5	2.241(4)
Cd1	O1[1]	2.370(4)	O4	Cd3[6]	2.247(5)
Cd1	O2	2.241(4)	O4	Cd3[8]	2.506(5)
Cd1	O6[2]	2.355(5)	O4	Na2	2.381(5)
Cd1	O8[2]	2.234(5)	O4	Na3[8]	2.506(5)
Cd1	O12[3]	2.348(4)	O4	Na3[6]	2.247(5)
Cd2	O1[2]	2.643(5)	O5	Cd5[10]	2.358(4)
Cd2	O2[4]	2.320(5)	O5	Na1[10]	2.358(4)
Cd2	O4	2.381(5)	O6	Cd1[2]	2.355(5)
Cd2	O8	2.313(5)	O6	Cd3[10]	2.603(4)
Cd2	O14[5]	2.349(4)	O6	Na3[10]	2.603(4)
Cd2	O15[6]	2.277(4)	O6	Na5[2]	2.355(5)
Cd3	O4[8]	2.506(5)	O7	Na6	2.275(5)
Cd3	O4[9]	2.247(5)	O8	Cd1[2]	2.234(5)
Cd3	O6[10]	2.603(4)	O8	Na2	2.313(5)
Cd3	O14[11]	2.384(5)	O8	Na5[2]	2.234(5)
Cd3	O15	2.329(5)	O9	Cd4[10]	2.396(5)
Cd3	O16	2.193(5)	O9	Cd5[12]	2.259(4)
Cd4	O5	2.403(4)	O9	Na1[12]	2.259(4)
Cd4	O7	2.163(5)	O10	Cd4[4]	2.221(4)
Cd4	O9[10]	2.396(5)	O10	Na6	2.746(5)
Cd4	O10[11]	2.221(4)	O10	Na1	2.317(4)
Cd4	O17[8]	2.536(4)	O11	Na4[10]	2.469(6)
Cd4	O18	2.176(5)	O11	Na6	2.214(5)
Cd5	O5[10]	2.358(4)	O11	Na1	2.197(4)
Cd5	O9[12]	2.259(4)	O12	Cd1[14]	2.348(4)
Cd5	O10	2.317(4)	O12	Na4[12]	2.900(6)
Cd5	O11	2.197(4)	O12	Na5[14]	2.348(4)
Cd5	O12	2.301(5)	O12	Na1	2.301(5)
Cd5	O17[5]	2.441(4)	O13	Na6[5]	2.569(5)

Na4	O5	2.848(6)	O14	Cd2[5]	2.349(4)
Na4	O6	2.477(5)	O14	Cd3[4]	2.384(5)
Na4	O9	2.309(5)	O14	Na2[5]	2.349(4)
Na4	O11[10]	2.469(6)	O14	Na6[5]	2.349(5)
Na4	O12[12]	2.900(6)	O14	Na3[4]	2.384(5)
Na4	O16[10]	2.475(5)	O15	Cd2[9]	2.277(4)
Na4	O17[13]	2.375(5)	O15	Na2[9]	2.277(4)
P1	O1	1.519(5)	O15	Na3	2.329(5)
P1	O3	1.607(5)	O16	Na4[10]	2.475(5)
P1	O5	1.523(5)	O16	Na6[8]	2.269(5)
P1	O6	1.510(5)	O16	Na3	2.193(5)
P2	O2	1.517(5)	O17	Cd4[8]	2.536(4)
P2	O3	1.623(5)	O17	Cd5[5]	2.441(4)
P2	O4	1.523(5)	O17	Na4[15]	2.375(5)
P2	O18	1.483(5)	O17	Na1[5]	2.441(4)
P3	O7	1.517(5)	Na2	O1[2]	2.643(5)
P3	O8	1.542(5)	Na2	O2[4]	2.320(5)
P3	O9	1.538(5)	Na2	O14[5]	2.349(4)
P3	O10	1.534(5)	Na2	O15[6]	2.277(4)
P4	O11	1.514(5)	Na6	O13[5]	2.569(5)
P4	O13	1.611(5)	Na6	O14[5]	2.349(5)
P4	O16	1.512(5)	Na6	O16[8]	2.269(5)
P4	O17	1.511(4)	Na3	O4[8]	2.506(5)
P5	O12	1.519(5)	Na3	O4[9]	2.247(5)
P5	O13	1.612(5)	Na3	O6[10]	2.603(4)
P5	O14	1.529(5)	Na3	O14[11]	2.384(5)
P5	O15	1.497(5)	Na5	O1[1]	2.370(4)
O1	Cd1[1]	2.370(4)	Na5	O6[2]	2.355(5)
O1	Cd2[2]	2.643(5)	Na5	O8[2]	2.234(5)
O1	Na2[2]	2.643(5)	Na5	O12[3]	2.348(4)
O1	Na5[1]	2.370(4)	Na1	O5[10]	2.358(4)
O1	Na5	2.510(4)	Na1	O9[12]	2.259(4)
O2	Cd2[11]	2.320(5)	Na1	O17[5]	2.441(4)
O2	Na2[11]	2.320(5)			

Symmetry transformations used to generate equivalent atoms:

(1) NMPP

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

[5]1-X,-Y,-1/2+Z; [6]1-X,1-Y,-3/2+Z; [7]1/2-X,-1/2+Y,1/2+Z; [8]+X,-1+Y,+Z;

[9]1-X,1-Y,1/2+Z; [10]1/2-X,1/2+Y,-1/2+Z; [11]1/2-X,-1/2+Y,-1/2+Z; [12]1-X,-Y,1/2+Z;

[13]+X,-1+Y,-1+Z; [14]-1/2+X,1/2-Y,1+Z; [15]+X,1+Y,+Z; [16]+X,1+Y,1+Z;

[17]1-X,1-Y,3/2+Z; [18]1/2-X,-1/2+Y,-3/2+Z; [19]1/2+X,1/2-Y,-1+Z

(2) NCPP

[1]2-X,1-Y,-Z; [2]1-X,1-Y,-Z; [3]1+X,+Y,-1+Z; [4]-1+X,+Y,+Z;

[5]-X,-Y,1-Z; [6]+X,+Y,-1+Z; [7]1-X,-Y,2-Z; [8]1-X,-Y,1-Z;

[9]+X,+Y,1+Z; [10]1-X,1-Y,1-Z; [11]1+X,+Y,+Z; [12]-X,1-Y,1-Z;

[13]+X,1+Y,+Z; [14]-1+X,+Y,1+Z; [15]+X,-1+Y,+Z

Table S5. Selected bond angles of NMPP and NCPP.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
			NMPP				
O4	P1	O1	106.23(19)	$O10^{1}$	Na2	$O8^{5}$	170.50(19)
O3	P1	O4	111.6(2)	$O4^{5}$	Na2	O4	167.02(11)
O3	P1	O1	102.2(2)	$O4^{5}$	Na2	$O8^{5}$	71.78(15)
O2	P1	O4	113.2(2)	$O7^{12}$	Na2	$O10^{1}$	74.99(14)
O2	P1	O3	112.9(2)	O7	Na2	$O10^{1}$	114.52(16)
O2	P1	O1	109.9(2)	$O7^{12}$	Na2	$O4^{5}$	119.05(15)
O14	P2	O12	114.1(2)	O7	Na2	$O4^{5}$	75.27(15)
O14	P2	O13	108.2(2)	$O7^{12}$	Na2	O4	70.64(14)
O12	P2	O13	102.64(18)	O7	Na2	O4	93.12(14)
O15	P2	O14	110.3(2)	O7	Na2	$O7^{12}$	158.92(19)
O15	P2	O12	108.5(2)	$O7^{12}$	Na2	$O8^{5}$	96.11(15)
O15	P2	O13	113.1(2)	O7	Na2	$O8^{5}$	72.79(14)
O6	P4	O1	105.1(2)	$O8^{5}$	Na2	O4	99.53(14)
O7	P4	O6	111.33(19)	O14	Na4	$O12^{4}$	139.95(16)
O7	P4	O1	106.9(2)	O14	Na4	$O11^{4}$	72.74(12)
O5	P4	O6	113.0(2)	O14	Na4	$O10^{15}$	127.19(16)
O5	P4	O7	114.4(2)	O14	Na4	$O6^{17}$	74.32(13)
O5	P4	O1	105.3(2)	O14	Na4	O13	60.32(13)
O11	P3	O9	102.61(19)	O14	Na4	$O9^{15}$	117.90(16)
O10	P3	O11	112.9(2)	$O12^{4}$	Na4	$O11^{4}$	74.84(14)
O10	P3	O9	107.2(2)	$O12^{4}$	Na4	$O10^{15}$	74.03(12)
O8	P3	O11	108.8(2)	$O12^{4}$	Na4	$O6^{17}$	69.93(13)
O8	P3	O10	111.1(2)	$O12^{4}$	Na4	O13	142.29(15)
O8	P3	O9	114.0(2)	$O11^{4}$	Na4	$O10^{15}$	146.09(16)
$O14^{1}$	Mg2	$O11^{10}$	88.99(17)	$O11^{4}$	Na4	$O6^{17}$	61.79(13)
$O14^{1}$	Mg2	$O9^{10}$	88.18(16)	$O11^{4}$	Na4	O13	89.97(13)
$O11^{10}$	Mg2	$O9^{10}$	67.56(13)	$O10^{15}$	Na4	$O6^{17}$	94.80(14)

O15	Mg2	$O14^{1}$	173.77(17)	O13	Na4	$O10^{15}$	123.24(15)
O15	Mg2	$O11^{10}$	96.26(17)	O13	Na4	$O6^{17}$	132.35(14)
O15	Mg2	$O6^{9}$	84.99(17)	$O9^{15}$	Na4	$O12^{4}$	102.10(14)
O15	Mg2	$O9^{10}$	96.91(16)	$O9^{15}$	Na4	$O11^{4}$	141.20(15)
O3	Mg2	$O14^{1}$	93.78(17)	$O9^{15}$	Na4	$O10^{15}$	59.87(13)
O3	Mg2	$O11^{10}$	166.17(16)	$O9^{15}$	Na4	$O6^{17}$	154.59(15)
O3	Mg2	O15	81.91(16)	$O9^{15}$	Na4	O13	68.70(13)
O3	Mg2	$O6^{9}$	115.05(15)	O14	Na3	O15	57.54(13)
O3	Mg2	$O9^{10}$	98.96(15)	O14	Na3	$O3^{9}$	158.15(16)
$O6^{9}$	Mg2	$O14^{1}$	92.83(16)	O14	Na3	$O1^{3}$	97.48(13)
$O6^{9}$	Mg2	$O11^{10}$	78.29(14)	O14	Na3	$O1^{9}$	115.49(15)
$O6^{9}$	Mg2	$O9^{10}$	145.81(16)	O14	Na3	$O5^{3}$	117.66(15)
$O12^{11}$	Mg1	$O13^{11}$	68.67(13)	O14	Na3	$O5^{17}$	86.27(15)
$O10^{1}$	Mg1	$O12^{11}$	91.10(16)	O15	Na3	$O1^{3}$	106.73(12)
$O10^{1}$	Mg1	O4	92.13(17)	$O3^{9}$	Na3	O15	132.93(16)
$O10^{1}$	Mg1	$O7^{12}$	84.68(17)	$O3^{9}$	Na3	$O1^{3}$	96.46(13)
$O10^{1}$	Mg1	$O13^{11}$	91.35(16)	$O3^{9}$	Na3	$O1^{9}$	57.42(13)
O4	Mg1	$O12^{11}$	164.55(16)	$O3^{9}$	Na3	$O5^{3}$	84.18(14)
O4	Mg1	$O7^{12}$	84.95(14)	$O3^{9}$	Na3	$O5^{17}$	77.69(14)
O4	Mg1	$O13^{11}$	96.15(15)	$O1^{9}$	Na3	O15	81.46(13)
$O7^{12}$	Mg1	$O12^{11}$	110.39(15)	$O1^{9}$	Na3	$O1^{3}$	144.03(12)
$O7^{12}$	Mg1	$O13^{11}$	175.92(19)	$O5^{17}$	Na3	O15	142.11(15)
O8	Mg1	$O12^{11}$	91.94(16)	$O5^{3}$	Na3	O15	78.39(13)
O8	Mg1	$O10^{1}$	171.03(17)	$O5^{3}$	Na3	$O1^{9}$	96.52(14)
O8	Mg1	O4	87.17(17)	$O5^{17}$	Na3	$O1^{3}$	87.24(14)
O8	Mg1	$O7^{12}$	86.35(17)	$O5^{17}$	Na3	$O1^{9}$	107.89(15)
O8	Mg1	$O13^{11}$	97.62(16)	$O5^{3}$	Na3	$O1^{3}$	53.19(12)
O12	Mg3	O11	96.43(17)	$O5^{3}$	Na3	$O5^{17}$	134.11(14)
O12	Mg3	$O6^{14}$	75.74(14)	$O15^{1}$	Na1	$O4^{1}$	121.90(15)
O12	Mg3	$O2^{3}$	91.93(15)	$O15^{1}$	Na1	$O3^{1}$	66.96(14)

O12	Mg3	$O13^{7}$	169.03(18)	$O15^{1}$	Na1	$O8^{1}$	150.13(16)
O12	Mg3	$O9^{4}$	85.32(15)	$O3^{1}$	Na1	$O4^{1}$	56.68(13)
O11	Mg3	$O6^{14}$	68.41(14)	$O3^{1}$	Na1	$O8^{1}$	117.27(15)
O11	Mg3	$O2^{3}$	83.12(15)	$O8^{1}$	Na1	$O4^{1}$	62.94(12)
O11	Mg3	$O13^{7}$	91.21(16)	O2	Na1	$O15^{1}$	89.45(15)
O11	Mg3	$O9^{4}$	171.98(17)	O2	Na1	$O4^{1}$	148.65(15)
$O2^{3}$	Mg3	$O6^{14}$	147.03(16)	O2	Na1	$O3^{1}$	152.49(16)
$O13^{7}$	Mg3	$O6^{14}$	99.96(14)	O2	Na1	$O8^{1}$	90.25(15)
$O13^{7}$	Mg3	$O2^{3}$	96.81(15)	O5	Na1	$O15^{1}$	88.31(15)
$O13^{7}$	Mg3	$O9^{4}$	86.05(17)	O5	Na1	$O4^{1}$	94.67(14)
$O9^{4}$	Mg3	$O6^{14}$	104.62(14)	O5	Na1	$O3^{1}$	80.05(14)
$O9^{4}$	Mg3	$O2^{3}$	104.68(16)	O5	Na1	$O8^{1}$	121.44(15)
$O10^{1}$	Na2	$O4^{5}$	115.24(16)	O5	Na1	O2	85.55(16)
$O10^{1}$	Na2	O4	74.60(13)				

NCPP

$O1^{1}$	Cd1	O1	81.62(15)	O5	P1	O3	107.0(3)
O2	Cd1	O1	81.15(15)	O6	P1	O1	114.4(3)
O2	Cd1	$O1^{1}$	82.41(16)	O6	P1	O3	104.0(3)
O2	Cd1	$O6^{2}$	83.81(16)	O6	P1	O5	111.0(3)
O2	Cd1	$O12^{3}$	80.18(16)	O2	P2	O3	107.0(3)
$O6^{2}$	Cd1	O1	106.03(14)	O2	P2	O4	111.4(3)
$O6^{2}$	Cd1	$O1^{1}$	163.01(15)	O4	P2	O3	103.3(3)
$O8^{2}$	Cd1	O1	88.47(16)	O18	P2	O2	111.4(3)
$O8^{2}$	Cd1	$O1^{1}$	97.66(16)	O18	P2	O3	109.5(3)
$O8^{2}$	Cd1	O2	169.51(16)	O18	P2	O4	113.7(3)
$O8^{2}$	Cd1	$O6^{2}$	97.69(16)	O7	P3	O8	112.3(3)
$O8^{2}$	Cd1	$O12^{3}$	110.29(16)	O7	P3	O9	110.1(3)
$O12^{3}$	Cd1	$O1^{1}$	84.40(15)	O7	P3	O10	105.6(3)
$O12^{3}$	Cd1	O1	157.96(15)	O9	P3	O8	108.9(3)
$O12^{3}$	Cd1	$O6^{2}$	83.49(15)	O10	P3	O8	110.4(3)

O2[4]	Cd2	O1[2]	75.22(15)	O10	P3	O9	109.3(3)
O2[4]	Cd2	O4	161.32(16)	O11	P4	O13	105.8(3)
O2[4]	Cd2	O14[5]	111.18(16)	O16	P4	O11	108.4(3)
O4	Cd2	O1[2]	94.88(15)	O16	P4	O13	110.8(3)
O8	Cd2	O1[2]	83.67(15)	O17	P4	O11	113.4(3)
O8	Cd2	O2[4]	95.71(16)	O17	P4	O13	104.6(3)
O8	Cd2	O4	98.93(16)	O17	P4	O16	113.5(3)
O8	Cd2	O14[5]	105.49(16)	O12	P5	O13	104.3(2)
O14[5]	Cd2	O1[2]	167.78(15)	O12	P5	O14	110.5(3)
O14[5]	Cd2	O4	75.94(16)	O14	P5	O13	102.0(2)
O15[6]	Cd2	O1[2]	76.84(15)	O15	P5	O12	115.5(3)
O15[6]	Cd2	O2[4]	83.50(16)	O15	P5	O13	108.5(3)
O15[6]	Cd2	O4	78.78(16)	O15	P5	O14	114.6(3)
O15[6]	Cd2	O8	160.05(17)	O2[4]	Na2	O1[2]	75.22(15)
O15[6]	Cd2	O14[5]	93.26(16)	O2[4]	Na2	O4	161.32(16)
O17[13]	Na4	O16[10]	94.19(18)	O2[4]	Na2	O14[5]	111.18(16)
O1	P1	O3	105.5(2)	O4	Na2	O1[2]	94.88(15)
O4[7]	Cd3	O4[9]	87.83(16)	O8	Na2	O1[2]	83.67(15)
O4[7]	Cd3	O6[10]	83.05(15)	O8	Na2	O2[4]	95.71(16)
O4[9]	Cd3	O6[10]	170.87(15)	O8	Na2	O4	98.93(16)
O4[7]	Cd3	O14[11]	109.21(16)	O8	Na2	O14[5]	105.49(16)
O4[7]	Cd3	O15	80.48(16)	O14[5]	Na2	O1[2]	167.78(15)
O12	Na1	O5[10]	87.67(16)	O14[5]	Na2	O4	75.94(16)
O12	Na1	O10	168.39(16)	O15[6]	Na2	O1[2]	76.84(15)
O14[11]	Cd3	O4[9]	72.98(15)	O15[6]	Na2	O2[4]	83.50(16)
O14[11]	Cd3	O6[10]	110.20(15)	O15[6]	Na2	O4	78.78(16)
O1	P1	O5	114.0(3)	O15[6]	Na2	O8	160.05(17)
O15	Cd3	O4[9]	93.72(16)	O15[6]	Na2	O14[5]	93.26(16)
O15	Cd3	O6[10]	84.65(15)	O7	Na6	O10	56.97(16)
O15	Cd3	O14[11]	162.77(16)	O7	Na6	O13[5]	134.95(18)

O12	Na1	$O17^{5}$	89.95(16)	O7	Na6	$O14^{5}$	118.7(2)
O16	Cd3	$O4^{9}$	99.62(16)	O11	Na6	O7	97.26(19)
O16	Cd3	$O4^{7}$	166.17(17)	O11	Na6	O10	78.09(16)
O16	Cd3	$O6^{10}$	89.28(16)	O11	Na6	$O13^{5}$	85.02(18)
O16	Cd3	$O14^{11}$	84.22(16)	O11	Na6	$O14^{5}$	140.96(19)
O16	Cd3	O15	87.38(16)	O11	Na6	$O16^{9}$	103.60(19)
O5	Cd4	$O17^{9}$	171.21(15)	$O13^{5}$	Na6	O10	79.97(15)
O7	Cd4	O5	99.48(17)	$O14^{5}$	Na6	O10	107.88(17)
O7	Cd4	$O9^{10}$	92.83(18)	$O14^{5}$	Na6	$O13^{5}$	59.32(15)
O7	Cd4	$O10^{11}$	167.62(17)	$O16^{9}$	Na6	O7	103.63(19)
O7	Cd4	$O17^{9}$	86.79(16)	$O16^{9}$	Na6	O10	160.36(18)
O7	Cd4	O18	91.81(19)	$O16^{9}$	Na6	$O13^{5}$	119.61(17)
$O9^{10}$	Cd4	O5	116.94(15)	$O16^{9}$	Na6	$O14^{5}$	83.37(17)
$O9^{10}$	Cd4	$O17^{9}$	68.53(14)	$O4^{7}$	Na3	$O4^{9}$	87.83(16)
$O10^{11}$	Cd4	O5	92.90(16)	$O4^{9}$	Na3	$O6^{10}$	170.87(15)
$O10^{11}$	Cd4	$O9^{10}$	81.26(16)	$O4^{7}$	Na3	$O6^{10}$	83.05(15)
$O10^{11}$	Cd4	$O17^{9}$	80.93(15)	$O4^{7}$	Na3	$O14^{11}$	109.21(16)
O18	Cd4	O5	88.66(16)	$O4^{7}$	Na3	O15	80.48(16)
O18	Cd4	$O9^{10}$	152.76(16)	$O14^{11}$	Na3	$O4^{9}$	72.98(15)
O18	Cd4	$O10^{11}$	88.69(17)	$O14^{11}$	Na3	$O6^{10}$	110.20(15)
O18	Cd4	$O17^{9}$	84.96(16)	O15	Na3	$O4^{9}$	93.72(16)
$O5^{10}$	Cd5	$O17^{5}$	170.55(15)	O15	Na3	$O6^{10}$	84.65(15)
$O9^{12}$	Cd5	$O5^{10}$	98.39(16)	O15	Na3	$O14^{11}$	162.77(16)
$O9^{12}$	Cd5	O10	82.23(16)	O16	Na3	$O4^{7}$	166.17(17)
$O9^{12}$	Cd5	O12	87.99(16)	O16	Na3	$O4^{9}$	99.62(16)
$O9^{12}$	Cd5	$O17^{5}$	72.38(15)	O16	Na3	$O6^{10}$	89.28(16)
O10	Cd5	$O5^{10}$	99.90(16)	O16	Na3	$O14^{11}$	84.22(16)
O10	Cd5	$O17^{5}$	81.15(15)	O16	Na3	O15	87.38(16)
O11	Cd5	$O5^{10}$	96.34(17)	$O1^{1}$	Na5	O1	81.62(15)
O11	Cd5	$O9^{12}$	163.75(17)	O2	Na5	$O1^{1}$	82.41(16)

O11	Cd5	O10	88.51(16)	O2	Na5	O1	81.15(15)
O11	Cd5	O12	99.47(16)	O2	Na5	O6[2]	83.81(16)
O11	Cd5	O17[5]	93.07(16)	O2	Na5	O12[3]	80.18(16)
O12	Cd5	O5[10]	87.67(16)	O6[2]	Na5	O1[1]	163.01(15)
O12	Cd5	O10	168.39(16)	O6[2]	Na5	O1	106.03(14)
O12	Cd5	O17[5]	89.95(16)	O8[2]	Na5	O1[1]	97.66(16)
O5	Na4	O12[12]	123.59(16)	O8[2]	Na5	O1	88.47(16)
O6	Na4	O5	55.50(15)	O8[2]	Na5	O2	169.51(16)
O6	Na4	O12[12]	70.73(16)	O8[2]	Na5	O6[2]	97.69(16)
O9	Na4	O5	93.28(17)	O8[2]	Na5	O12[3]	110.29(16)
O9	Na4	O6	94.54(18)	O12[3]	Na5	O1[1]	84.40(15)
O9	Na4	O11[10]	140.2(2)	O12[3]	Na5	O1	157.96(15)
O9	Na4	O12[12]	73.93(17)	O12[3]	Na5	O6[2]	83.49(15)
O9	Na4	O16[10]	155.6(2)	O5[10]	Na1	O17[5]	170.55(15)
O9	Na4	O17[13]	72.79(17)	O9[12]	Na1	O5[10]	98.39(16)
O11[10]	Na4	O5	79.01(16)	O9[12]	Na1	O10	82.23(16)
O11[10]	Na4	O6	111.65(19)	O9[12]	Na1	O12	87.99(16)
O11[10]	Na4	O12[12]	141.95(19)	O9[12]	Na1	O17[5]	72.38(15)
O11[10]	Na4	O16[10]	59.52(16)	O10	Na1	O5[10]	99.90(16)
O16[10]	Na4	O5	106.90(17)	O10	Na1	O17[5]	81.15(15)
O16[10]	Na4	O6	86.16(18)	O11	Na1	O5[10]	96.34(17)
O16[10]	Na4	O12[12]	83.41(17)	O11	Na1	O9[12]	163.75(17)
O17[13]	Na4	O5	150.5(2)	O11	Na1	O10	88.51(16)
O17[13]	Na4	O6	148.7(2)	O11	Na1	O12	99.47(16)
O17[13]	Na4	O11[10]	95.05(18)	O11	Na1	O17[5]	93.07(16)
O17[13]	Na4	O12[12]	78.25(17)				

Symmetry transformations used to generate equivalent atoms:

(1) NMPP

[1]+X,+Y,-1+Z; [2]1-X,1-Y,-1/2+Z; [3]+X,+Y,1+Z; [4]1/2-X,1/2+Y,1/2+Z;
[5]1-X,-Y,-1/2+Z; [6]1-X,1-Y,-3/2+Z; [7]1/2-X,-1/2+Y,1/2+Z; [8]+X,-1+Y,+Z;
[9]1-X,1-Y,1/2+Z; [10]1/2-X,1/2+Y,-1/2+Z; [11]1/2-X,-1/2+Y,-1/2+Z; [12]1-X,-Y,1/2+Z;

[13]+X,-1+Y,-1+Z; [14]-1/2+X,1/2-Y,1+Z; [15]+X,1+Y,+Z; [16]+X,1+Y,1+Z;

[17]1-X,1-Y,3/2+Z; [18]1/2-X,-1/2+Y,-3/2+Z; [19]1/2+X,1/2-Y,-1+Z

(2) NCPP

[1]2-X,1-Y,-Z; [2]1-X,1-Y,-Z; [3]1+X,+Y,-1+Z; [4]-1+X,+Y,+Z;

[5]-X,-Y,1-Z; [6]+X,+Y,-1+Z; [7]1-X,-Y,2-Z; [8]1-X,-Y,1-Z;

[9]+X,+Y,1+Z; [10]1-X,1-Y,1-Z; [11]1+X,+Y,+Z; [12]-X,1-Y,1-Z;

[13]+X,1+Y,+Z; [14]-1+X,+Y,1+Z; [15]+X,-1+Y,+Z

Table S6. The cut-off edges for the reported mixed P-O anion phosphates.

	Compound	Space group	P-O group	Cut-off edge	Ref.
1	$Na_6Sr_2Bi_3(PO_4)(P_2O_7)_4$	$P\bar{4}2_1c$	PO_4, P_2O_7	260	11
2	$Cs_2CaBi_2(PO_4)_2(P_2O_7)$	$P2_1/c$	PO_4, P_2O_7	270	11
3	**$Na_3Cd_4(PO_4)(P_2O_7)_2$**	***P*$\bar{1}$**	**PO_4, P_2O_7**	**＜190**	This work
4	**$Na_4Mg_3(PO_4)_2(P_2O_7)$**	***Pna*2_1**	**PO_4, P_2O_7**	**＜190**	This work
5	$Li_{1.52}Na_{4.48}Cd_8(PO_4)_2(P_2O_7)_4$	$P\bar{1}$	PO_4, P_2O_7	230	12
6	$RbCd_6(P_2O_7)_2P_3O_{10}$	$P2_1/m$	P_2O_7, P_3O_{10}	200	13
7	$Pb_2Ba_7(Li_2(P_2O_7)_2(P_4O_{13})_2)$	$P\bar{1}$	P_2O_7, P_4O_{13}	240	14
8	$Pb_3Ba_6(Li_2(P_2O_7)_2(P_4O_{13})_2)$	$P\bar{1}$	P_2O_7, P_4O_{13}	245	14
9	$K_2PbBi_2(PO_4)_2(P_2O_7)$	*Pnma*	PO_4, P_2O_7	270	15
10	$Rb_2CdBi_2(PO_4)_2(P_2O_7)$	$P2_1/c$	PO_4, P_2O_7	260	15
11	$Rb_2PbBi_2(PO_4)_2(P_2O_7)$	*Pnma*	PO_4, P_2O_7	289	16
12	$Cs_2PbBi_2(PO_4)_2(P_2O_7)$	*Pnma*	PO_4, P_2O_7	291	16
13	$Cs_2SrBi_2(PO_4)_2(P_2O_7)$	$P2_1/c$	PO_4, P_2O_7	287	17
14	$Rb_2CaBi_2(PO_4)_2(P_2O_7)$	$P2_1/c$	PO_4, P_2O_7	265	18
15	$Cs_6Bi_4(PO_4)_2(P_2O_7)_3$	$P2_1/c$	PO_4, P_2O_7	285	19
16	$RbCs_5Bi_4(PO_4)_2(P_2O_7)_3$	$P2_1/c$	PO_4, P_2O_7	280	19
17	$KCs_5Bi_4(PO_4)_2(P_2O_7)_3$	$P2_1/c$	PO_4, P_2O_7	284	19
18	$KCd_3PO_4(P_2O_7)$	$P2_1/m$	PO_4, P_2O_7	200	20
19	$KCd_6(P_2O_7)_2P_3O_{10}$	*Pbcm*	P_2O_7, P_3O_{10}	200	20
20	$Pb_2Cd_3(PO_4)_2(P_2O_7)$	$P\bar{1}$	PO_4, P_2O_7	243	21
21	$Rb_5Bi_5(PO_4)_4(P_2O_7)_2$	$P2_1/c$	PO_4, P_2O_7	280	22
22	$Cs_3Sr_2P_7O_{21}$	*C2/c*	P_4O_{12} rings, $^1[PO_3]_\infty$ chains	260	23

Table S7. Calculation of the dipole moments for the MgO_6 and PO_4 groups in NMPP.

Species			Dipole moments			
			x (a)	*y* (b)	*z* (c)	Magnitude
						Debye
Mg	$Mg(1)O_6$		-0.53	-0.50	-0.91	1.16
			0.53	-0.50	-0.91	1.16
			0.53	-0.50	0.91	1.16
			-0.53	-0.50	0.91	1.16
			0.53	-0.50	-0.91	1.16
			-0.53	-0.50	0.91	1.16
	$Mg(2)O_6$		2.02	-4.26	1.38	4.92
			-2.01	-4.26	1.38	4.91
			-2.01	-4.26	-1.38	4.91
			2.02	-4.26	-1.38	4.92
	$Mg(3)O_6$		-5.20	0.76	-1.47	5.46
			-5.20	0.76	-1.47	5.46
			5.20	0.76	-1.47	5.46
			5.20	0.76	1.47	5.46
			-5.20	0.76	1.47	5.46
			5.20	0.76	1.47	5.46
	Sum		**0**	**-15.48**	**0**	**15.48**
P	$P(1)O_4$		0.00	1.32	0.00	1.32
	$P(2)O_4$		0.00	-1.92	0.00	1.92
	Sum		**0**	**-0.6**	**0**	**0.6**
	P_2O_7	$P(3)O_4$	0.01	0.98	0.00	0.98
		$P(4)O_4$	-0.01	11.68	0.00	11.68
	Sum		**0**	**12.66**	**0**	**12.66**

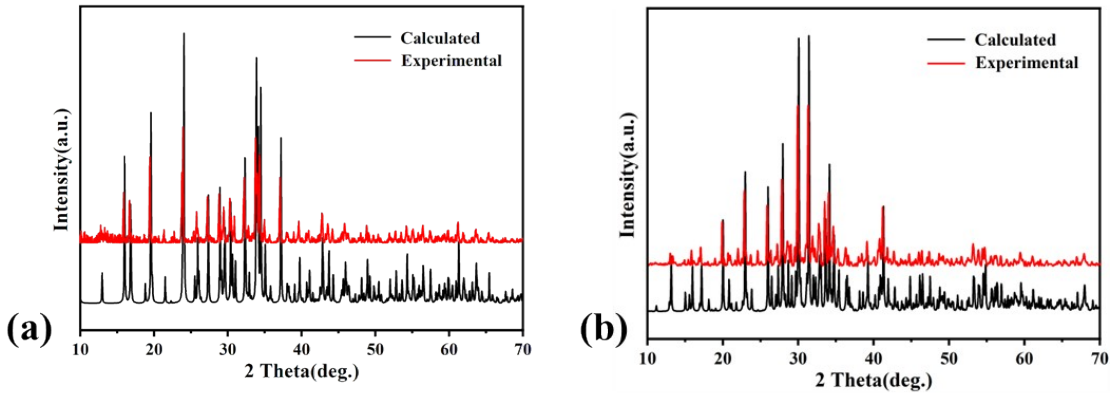

Fig. S1 The powder XRD patterns of (a) NMPP and (b) NCPP.

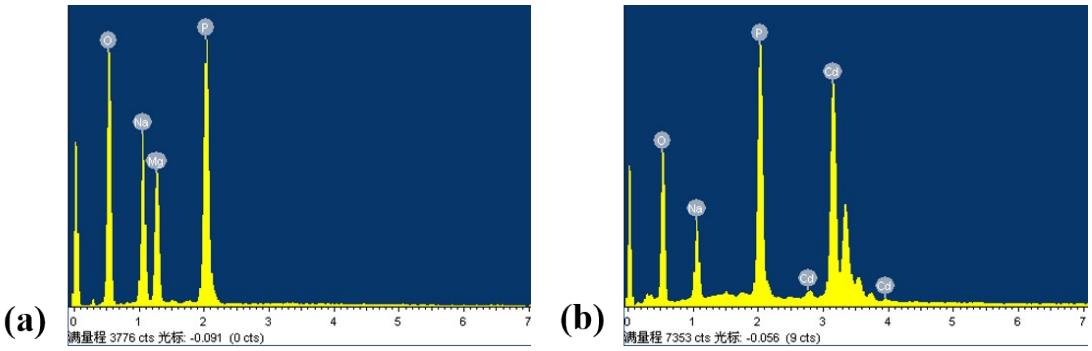

Fig. S2 EDS spectra of (a) NMPP and (b) NCPP.

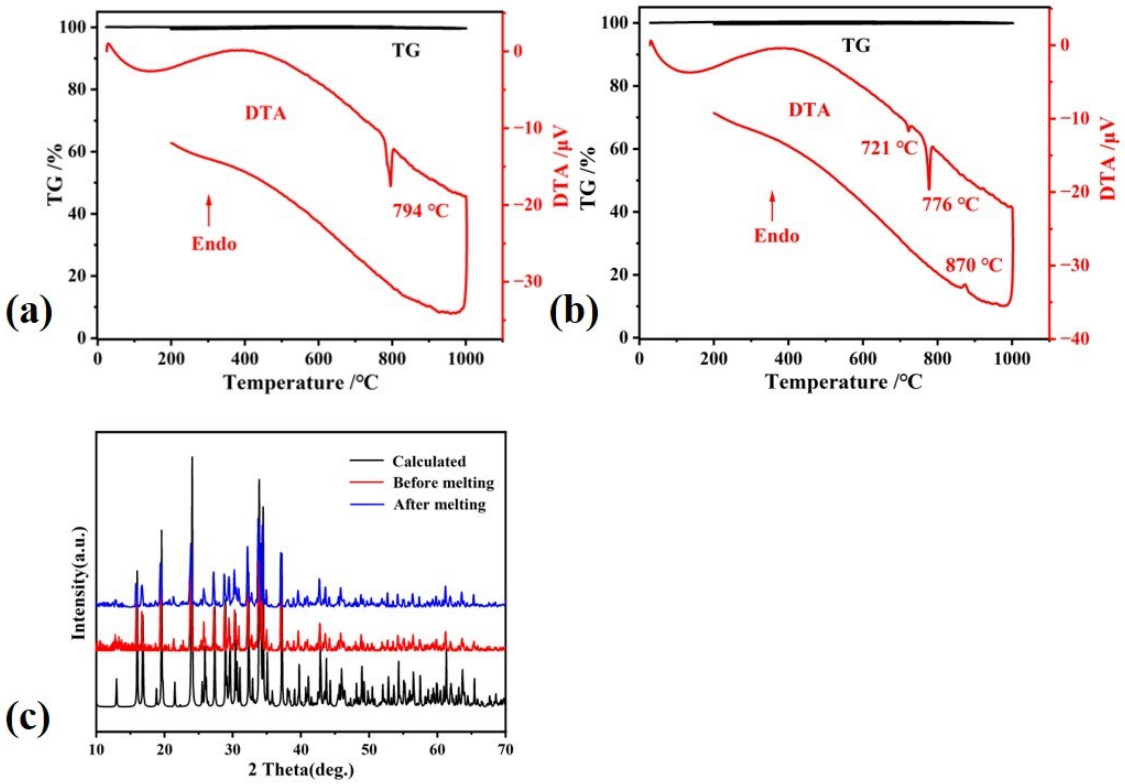

Fig. S3 TG-DTA curves of (a) NMPP and (b) NCPP, and XRD patterns of (c) NMPP before and after melting.

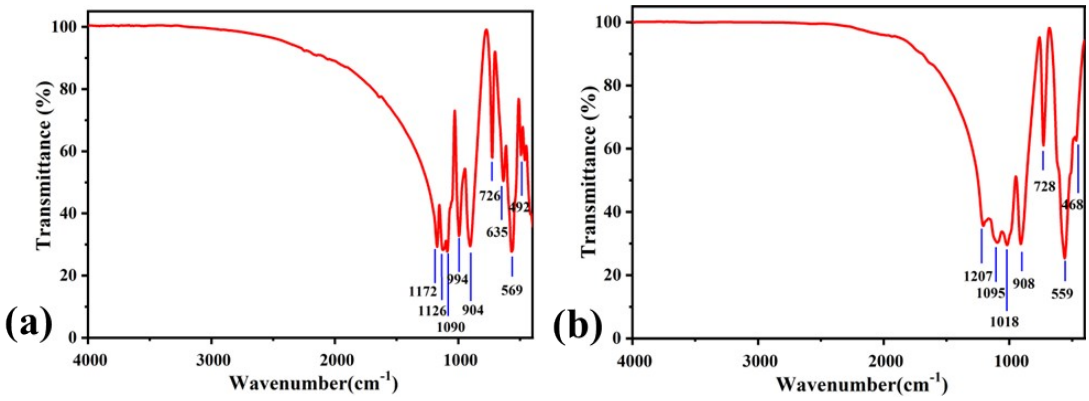

Fig. S4 IR spectra of (a) NMPP and (b) NCPP.

References

1. Bruker APEX2, *Inc.: Madison,* WI, 2005.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann*, J. Appl. Crystallogr.,* 2009, **42**, 339–341.
3. A. L. Spek, *J. Appl. Crystallogr.,* 2003, **36**, 7–13.
4. G. Kortüm, W. Braun and G. Herzog, *Angew. Chem., Int. Ed.,* 1963, **2**, 333–341.
5. S. K. Kurtz and T. T. Perry, *J. Appl. Phys.,* 1968, 39, 3798–3813.
6. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson and M. C. Payne, *Z. Kristallogr.,* 2005, **220**, 567–570.
7. A. J. Morris, R. J. Nicholls, C. J. Pickard and J. R. Yates, *Comput. Phys. Commun.,* 2014, **185**, 1477-1485.
8. R. J. Nicholls, A. J. Morris, C. J. Pickard and J. R. Yates, *J. Phys.: Conf. Ser.,* 2012, **371**, 012062.
9. J. Lin, M. Lee, Z. Liu, C. Chen and C. J. Pickard, *Phys. Rev. B.,* 1999, 60, 13380-13389.
10. X. Cheng, M.-H. Whangbo, G. Guo, M. Hong and S. Deng, *Angew. Chem., Int. Ed.,* 2018, **57**, 3997–4001.
11. Y. Yan, H. Yu, B. Zhou, Z. Hu, J. Wang, Y. Wu and H. Wu, *Inorg. Chem.*, 2023, **62**, 8064–8068.
12. Y. Fang, Z. Chen, Y. Shi, W. Zhang and X. Dong, *Inorg. Chem. Commun.*, 2017, **86**, 253–257.
13. Z. M. Lin, *J. Synth. Cryst.*, 2018, **47**, 1990–1994.
14. X. Zhang, H. Wu, Q. Liu, X. Dong, Y. Chen, Z. Yang, X, Wen and S. Pan, *Dalton Trans.*, 2017, **46**, 4678–4684.
15. Q. Lu, Z. Chen, L. Li, Q. Jing, N. Li, Z. Jiang, X. Dong and M.H. Lee, *Eur. J. Inorg. Chem.*, 2020, **2020**, 4007–4014.
16. M. Wen, H. Wu and X. Wu, *Inorg. Chem.*, 2020, **59**, 2945–2951.
17. S. Guo, P. Chen, L. Song, P. Guo and J. Gao, *J. Solid State Chem.*, 2020, **288**, 121411.
18. H. Wu and Y. Shen, *J. Solid State Chem.*, 2022, **315**, 123471.
19. S. Liu, J. Chen, H. Wu, H. Yu, Z. Hu, J. Wang and Y. Wu, *Inorg. Chem. Front.*, 2021, **8**, 5270–5276.
20. B. Cai, D. Dou, B. Zhang, L. Li and Y. Wang, *Dalton Trans.*, 2023, **52**, 862–865.
21. W. Chen, Q. Jing, Q. Zhang, M.-H. Lee, X. Lu, P. Wei and Z. Chen, *Eur. J. Inorg. Chem.*, 2019, **2019**, 1273–1278.
22. R. Liu, H. Wu, H. Yu, Z. Hu, J. Wang and Y. Wu, *J. Alloys Compd.*, 2022, **896**, 163066.
23. M. Abudoureheman, S. Han, Y. Wang, B. H. Lei, Z. Yang and S. Pan, *Inorg. Chem.*, 2017, **56**, 3939–3945.