$[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$: A new metal-free ultraviolet nonlinear optical phosphate with large birefringence and second-harmonic generation response

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ABSTRACT $[\text{PO}_4]^{3-}$ possesses small microscopic second-order susceptibility and polarizability anisotropy, which inherently result in weak second-harmonic generation (SHG) and small birefringence. Herein, a new noncentrosymmetric phosphate, $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$, was successfully designed and synthesized by a solution evaporation method. $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ without metal ions is composed of planar conjugated guanidine cations and PO_4 tetrahedrons, which are connected by hydrogen bonds, forming a three-dimensional network. Physical property measurements indicate that the title compound displays an SHG response of $1.5 \times \text{KH}_2\text{PO}_4$ (KDP) and a larger birefringence (0.055@546.1 nm) compared with most reported ultraviolet nonlinear optical phosphates. Furthermore, first-principles calculations reveal that the π -conjugated planar $[\text{C}(\text{NH}_2)_3]^+$ cations and $[\text{PO}_4]^{3-}$ groups are responsible for its excellent linear and NLO properties.

Keywords: nonlinear optical material, second-harmonic generation, birefringence, structure-property relationship

INTRODUCTION

Ultraviolet (UV) nonlinear optical (NLO) crystals have always been one of the hotspots in scientific research due to their pivotal role in UV solid-state laser systems [1–3]. For an excellent UV NLO material, moderate birefringence and large second-harmonic generation (SHG) response are essential to realize phase-matching (PM) in the desired wavelength range and obtain high laser conversion efficiency. Therefore, it is still urgently demanded to design UV NLO materials possessing both traits.

Traditionally, the search for high-performance optical materials was mainly focused on inorganic π -conjugated systems including borates, carbonates, and nitrates, because of their outstanding hyperpolarizabilities and anisotropies. The continuous studies on these π -conjugated systems have resulted in the findings of many excellent UV NLO materials, such as $\beta\text{-Rb}_2\text{Al}_2\text{B}_2\text{O}_7$ [4], $\text{NH}_4\text{B}_4\text{O}_6\text{F}$ [5], $\text{Ca}_2\text{B}_{10}\text{O}_{14}\text{F}_6$ [6], ABCO_3F (A = K, Rb, Cs; B = Ca, Sr) [7] and $\text{Re}(\text{NO}_3)\text{OH}$ (Re = La, Y, Gd) [8].

In recent years, besides the π -conjugated systems, non- π -conjugated systems are considered as rich exploration systems for NLO materials attributable to their remarkable resistant absorption, diversity of noncentrosymmetric crystal structures, and easy growth of large single crystals [9–14]. Among the non- π -conjugated systems, phosphates have attracted much attention because of their strong rigidity, which contributes to improving the thermal and chemical stabilities [15]. So far, many UV NLO phosphates have been reported, such as $\text{Ba}_3\text{P}_3\text{O}_{10}\text{X}$ (X = Cl, Br) ($0.6 \times \text{KDP}$, $0.023@1064\text{nm}$, $\text{KDP} = \text{KH}_2\text{PO}_4$) [16], LiPbPO_4 ($3 \times \text{KDP}$, $0.021@1064\text{nm}$) [17], $\text{K}_4\text{Mg}_4(\text{P}_2\text{O}_7)_3$ ($1.3 \times \text{KDP}$, $0.0108@1064\text{nm}$) [18], $\text{Rb}_4\text{Mg}_4(\text{P}_2\text{O}_7)_3$ ($1.4 \times \text{KDP}$, $0.009@1064\text{nm}$) [18], $\text{NaNH}_4\text{PO}_3\text{F} \cdot \text{H}_2\text{O}$ ($1.1 \times \text{KDP}$, $0.053@589\text{nm}$) [19], and $(\text{NH}_4)_2\text{PO}_3\text{F}$ ($1 \times \text{KDP}$, $0.027@1064\text{nm}$) [20]. Although most of them have impressive short cut-off UV edges, they show either weak SHG responses or small birefringence, which hinders their conversion efficiency and PM abilities [21]. To date, to enhance the SHG effect of UV NLO phosphates, some strategies have been developed, such as constructing strong distortion in the

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[Mg₄P₆O₂₁] double layer of M₄Mg₄(P₂O₇)₃ (M = K, Rb) (1.3–1.4 × KDP), condensing [PO₄]^{3−} units in RbBa₂(PO₃)₅ (1.4 × KDP), and aligning nonbonding O-2p orbitals in LiCs₂PO₄ (2.8 × KDP) [22]. However, these strategies only effectively enhanced the SHG responses but did not improve the birefringence of phosphates. Another effective design strategy is to introduce stereochemically active d⁰ or ns² lone pair cations [23,24]. These second-order Jahn-Teller (SOJT) cations could enhance the SHG response and/or birefringence. According to this method, some phosphates have been produced, such as Rb₃PbBi(P₂O₇)₂, Cs₃PbBi(P₂O₇)₂, and K₂Sb(P₂O₇)F. However, this approach may be accompanied with undesired red shift possibilities. A classic example is the KTiOPO₄ (KTP), which exhibits very strong SHG response and moderate birefringence due to the aligned arrangement of the SOJT-distorted TiO₆ octahedra. However, the cut-off edge of KTP is only 350 nm [25,26]. Therefore, it is still necessary to develop an effective strategy to design UV phosphates with enhanced SHG response, moderate birefringence, and short UV cut-off edge.

It is well-known that the delocalized π -conjugated groups, such as (BO₃)^{3−}, (CO₃)^{2−} and (NO₃)[−], having large hyperpolarizability, strong anisotropy, and wide band gap, are ideal fundamental building units (FBUs) for UV NLO materials [27–32]. In addition to these π -conjugated anionic groups, the π -conjugated [C(NH₂)₃]⁺ cationic group is expected to have similar optical properties due to similar isoelectronic structures. Additionally, metal-free [C(NH₂)₃]⁺ has less negative effect on the UV cut-off edge than metal cations. Previously, our group combined the π -conjugated [C(NH₂)₃]⁺ cationic units with [SO₃F][−] units to synthesize an excellent UV NLO crystal, C(NH₂)₃SO₃F [33]. The study revealed that its superior linear and non-linear optical properties are derived from the well arrangement of π -conjugated [C(NH₂)₃]⁺ cationic group. Moreover, the growth of traditional inorganic NLO crystals commonly needs high cost and energy consumption. Based on the principle of environmental friendliness, energy saving and economic benefit, the non-toxicity and low-cost metal-free NLO material is more in line with the requirements of the times. Given these ideas above, in this work, we introduced the π -conjugated [C(NH₂)₃]⁺ into phosphate to enhance its SHG responses and birefringence, while retaining the inherent advantages of phosphate. Herein, a new metal-free phosphate, [C(NH₂)₃]₃PO₄·2H₂O, has been obtained. [C(NH₂)₃]₃PO₄·2H₂O has the remarkable SHG effect (1.5 × KDP), large birefringence (0.055@546 nm) as well as

short UV cut-off edge ($\lambda_{\text{cut-off}} = 250$ nm). We report the synthesis, crystal structure, and NLO properties of this new metal-free phosphate, and reveal the origin of its optical properties by first-principles calculations.

EXPERIMENTAL SECTION

Reagents

All of the chemical reagents were analytical grade and were used with no further treatment. C(NH₂)₃H₂PO₄ (Aladdin, 99.9%) and H₃PO₄ (Aladdin, 85%) were used without further purification.

Synthesis

Single crystals of [C(NH₂)₃]₃PO₄·2H₂O were synthesized by slowly evaporating (CN₃H₆)H₂PO₄ (0.523 g, 3.3 mmol) in H₃PO₄ solution at room temperature. Colorless block crystals were obtained after several days (Fig. S1).

Single crystal structure determination

X-ray diffraction (XRD) of [C(NH₂)₃]₃PO₄·2H₂O was performed on a Bruker P4 diffractometer equipped with Mo-K α radiation ($\lambda = 0.71073$ Å) at 293 K. Utilizing Olex2 [34], the structure was solved and refined by ShelXT and ShelXL, respectively. The structure was verified by Platon and no higher symmetry was found [35]. Crystallographic data and structural refinements are listed in Table 1. Atomic coordinates, equivalent isotropic displacement parameters, anisotropic displacement parameters, and basic information for [C(NH₂)₃]₃PO₄·2H₂O are listed in Tables S1–S5, respectively.

Powder XRD (PXRD) patterns of polycrystalline materials were collected on a Miniflex600 powder X-ray diffractometer with Cu K α radiation ($\lambda = 1.540598$ Å) at room temperature in the range of $2\theta = 5^\circ$ – 75° with a fixed time of 0.2 s. The phase purity was checked, and no impurities were observed. The PXRD pattern of [C(NH₂)₃]₃PO₄·2H₂O was consistent with the calculated XRD pattern from the single-crystal model (Fig. S2).

Energy-dispersive X-ray spectroscopy (EDS) analysis

The EDS analysis of [C(NH₂)₃]₃PO₄·2H₂O crystal was performed on a field emission scanning electron microscope (FESEM, SU-8010) equipped with an energy dispersive X-ray spectrometer (Fig. S3).

UV-Vis-NIR diffuse-reflectance spectrum

The UV-Vis-NIR diffuse reflectance spectrum of [C(NH₂)₃]₃PO₄·2H₂O was recorded on a Perkin-Elmer Lambda-950 UV/Vis/NIR spectrophotometer in

Table 1 Crystal data and structure refinements of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$

Formula	$[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$
Formula weight	311.26
Temperature (K)	293(2)
λ (Å)	0.71073
Crystal system	Orthorhombic
Space group	$Pna2_1$
a (Å)	14.6176(2)
b (Å)	8.8939(10)
c (Å)	11.5030(2)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å ³)	1495.48(4)
Z	4
ρ (calcd) (g cm ⁻³)	1.382
μ (mm ⁻¹)	0.222
$F(000)$	664.0
θ (deg)	2.681–27.519
Index range	$-18 \leq h \leq 18$ $-11 \leq k \leq 11$ $-14 \leq l \leq 14$
Reflections collected/unique	20288/3388
R_{int}	0.0345
Completeness to $\theta = 25.242^\circ$	100.0%
GOF on F^2	1.095
R_1/wR_2 [$F_o^2 > 2\sigma(F_o^2)$] ^a	0.0393 / 0.0984
R_1/wR_2 (all data)	0.0408 / 0.0997
Flack parameter	0.06(14)

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

200–1400 nm at room temperature using BaSO_4 as the standard of 100% reflectance. The absorption spectrum was calculated from the reflectance spectrum using the Kubelka–Munk function: $F(R) = (1 - R)^2/2R = K/S$, where R is the diffuse reflectance, K is the absorption coefficient, and S is the scattering coefficient [36,37].

Thermal analysis

Thermogravimetric analysis (TGA) was performed on an NETZSCH STA 449F3 instrument. The crystal sample was heated in the temperature range of 30–1200°C at a heating rate of 10°C min⁻¹.

SHG measurement

The SHG effects of the powder samples were measured by

using a modified Kurtz and Perry method with a Q-switched 1064 nm Nd:YAG laser [38]. The $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ samples were ground and divided into fractions according to different particle size ranges: 25–45, 45–62, 62–75, 75–109, 109–150, 150–220, 220–275, and 275–345 μm . KDP with the same particle size served as the standard.

First-principles computational methods

The first-principles calculations for $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ were performed by CASTEP [39] based on the density functional theory (DFT) [40]. The exchange-correlation energy was described by Perdew–Burke–Ernzerhof (PBE) in the generalized gradient approximation (GGA). The effective interactions between the atom cores and valence electrons were described by the norm-conserving pseudopotentials [41]. The valences of composed atoms were as follow: C $2s^2 2p^2$, N $2s^2 2p^3$, O $2s^2 2p^4$, P $3s^2 3p^3$, H $1s^1$. The cut-off energy for the plane wave basis was set to be 750 eV. The numerical integration of the Brillouin zone was performed using a Monkhorst–Pack scheme k -point grid density of $1 \times 1 \times 1$. In addition, the scissors operation was adopted owing to the underestimation of band gap [42].

RESULTS AND DISCUSSION

Crystal structure

$[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ crystallizes in the acentric orthorhombic space group of $Pna2_1$ (No.33) with cell parameters $a = 14.6176(2)$ Å, $b = 8.8939(10)$ Å, $c = 11.5030(2)$ Å and $Z = 4$. The asymmetric unit consists of three independent guanidine cations, one phosphate group, and two water molecules. There are strong hydrogen bonds between the guanidine and phosphate groups in the structure, forming a three-dimensional network.

For the organic cations of guanidine, the C atom is coordinated to three amino groups with C–N bond lengths in the range of 1.310–1.335 Å and the C–N–C bond angles in the range of 119.2°–121.0°, which makes the guanidine cations roughly shaped like a propeller (Fig. 1a). All $[\text{C}(\text{NH}_2)_3]^+$ cationic groups are inclined to the c axis in approximately the same direction, which makes a positive contribution to NLO susceptibilities. In terms of PO_4 tetrahedral groups, the bond lengths of P–O are in the range of 1.5108(19)–1.597(2) Å. It is noteworthy that all PO_4 tetrahedral groups are quite neatly arranged along the c axis. However, it is regrettable that the PO_4 tetrahedra and $[\text{C}(\text{NH}_2)_3]^+$ planar triangles are almost arranged oppositely along the c direction (Fig. 1b),

Figure 1 View of the crystal structure of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$: (a) planar trigonal $[\text{C}(\text{NH}_2)_3]^+$ and $[\text{PO}_4]^{3-}$ tetrahedra; (b) crystal structure along the b -axis.

which cancels part of the d_{33} contribution from the $[\text{C}(\text{NH}_2)_3]^+$ groups.

Thermogravimetric and stability analysis

$[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ shows no decomposition and hygroscopicity after being placed at room temperature in air for two weeks, and is insoluble in ethanol or acetone. The thermal behaviour of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ was investigated and the results are shown in Fig. S4. $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ started to decompose at 100°C followed by an endothermic dehydration weight loss (9.98%) of water molecule (H_2O). The endothermic peaks observed at 250 and 390°C in differential thermal analysis (DTA), in association with a weight loss (17.34%) of CH_4 as observed in thermogravimetric analysis (TGA), could be ascribed to the absorption of energy for the breakage of bonds in guanidine group [43]. The next stage of weight loss started at 600°C for the removal of about 46.88% N_2 and NH_3 as gaseous products evidenced by two endothermic peaks observed at 812 and 960°C . The compound was finally decomposed into P_2O_5 with a residual mass of 25.51% (cal. 22.83%) under the flowing nitrogen gas. Based on the results of TGA and DTA, the maximum temperature for NLO application of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ is limited to 100°C .

UV-Vis-IR diffuse-reflectance spectroscopy and birefringence

UV-Vis-NIR diffuse reflectance spectrum of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ in the region of 200–1200 nm was collected. It is clear that $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ has a relatively wide transmittance range and exhibits a large band gap of 4.2 eV (Fig. 2).

The birefringence of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ was measured with a ZEISS Axio A1 polarizing microscope (Fig. S5). The formula for calculating birefringence is as follows: $\Delta R = (|N_e - N_o|) \times T = \Delta n \times T$; ΔR , Δn and T

Figure 2 The UV-Vis-NIR diffuse reflectance spectrum of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$.

represent the optical path difference, birefringence, and thickness of a crystal, respectively. A single crystal was used for the birefringence measurement. The retardation was approximately 267.4 nm, and the thickness was $4.85 \mu\text{m}$. Hence, the experimental birefringence value of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ was $0.055@546.1 \text{ nm}$. This value is larger than those of most reported phosphates, especially those metal-free phosphates, such as $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) ($0.0394@1064 \text{ nm}$), $(\text{NH}_4)_2\text{PO}_3\text{F}$ ($0.027@1064 \text{ nm}$), and $[\text{C}(\text{NH}_2)_3]_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ ($0.014@532 \text{ nm}$) [50] (shown in Table 2). It is well-known that the polarizability anisotropy of the $(\text{PO}_4)^{3-}$ tetrahedron is much smaller than that of planar π -conjugated groups. Therefore, the enlarged birefringence of the title compound should originate from the contribution of the introduced planar $[\text{C}(\text{NH}_2)_3]^+$ cationic groups.

NLO properties

As shown in Fig. 3, $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ is type I phase-match and the SHG efficiency is roughly 1.5 times that of KDP. Notably, the SHG response of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ is larger than those of most reported UV NLO phosphates and pyrophosphates, such as $\text{Ba}_2\text{NaClP}_2\text{O}_7$ ($0.9 \times \text{KDP}$) [51], $\text{AMgPO}_4 \cdot 6\text{H}_2\text{O}$ ($A = \text{Rb}, \text{Cs}$) ($0.92\text{--}1.36 \times \text{KDP}$) [52], $\text{Na}_3\text{Sc}_2(\text{PO}_4)_2\text{F}_3$ ($0.26 \times \text{KDP}$), $\text{RbBa}_2(\text{PO}_3)_5$ ($1.4 \times \text{KDP}$), $\text{KLa}(\text{PO}_3)_4$ ($0.7 \times \text{KDP}$), $\text{Ba}_3\text{P}_3\text{O}_{10}\text{Cl}$ ($0.6 \times \text{KDP}$), and $\text{K}_4\text{Mg}_4(\text{P}_2\text{O}_7)_3$ ($1.3 \times \text{KDP}$) (in Table 2).

The relationship between structure and NLO properties

To further elucidate the relationship between the NLO properties and structure, the SHG contribution of $[\text{C}(\text{NH}_2)_3]^+$ and $[\text{PO}_4]^{3-}$ groups have been calculated based on the anionic group theory. Since the anionic group theory was proposed, it has been widely applied

Table 2 Optical properties for some UV NLO phosphates

Compound	Space group	Cut-off edge (nm)	SHG ($\times$ KDP)	Birefringence	Reference
RbBa ₂ (PO ₃) ₅	<i>Pc</i>	163	1.4	n/a ^a	[9]
KLa(PO ₃) ₄	<i>P2</i> ₁	<162	0.7	0.0084@1064nm	[44]
CsLa(PO ₃) ₄	<i>P2</i> ₁	<167	0.5	0.0068@1064nm	[45]
KPb ₂ (PO ₃) ₅	<i>Pn</i>	177	0.5	n/a	[46]
RbPb ₂ (PO ₃) ₅	<i>Pn</i>	163	0.3	n/a	[46]
Ba ₃ P ₃ O ₁₀ Cl	<i>Pca2</i> ₁	180	0.6	0.028@1064nm	[14]
Ba ₃ P ₃ O ₁₀ Br	<i>P2</i> ₁ 2 ₁ 2 ₁	<200	0.5	0.023@1064nm	[14]
Rb ₂ Ba ₃ (P ₂ O ₇) ₂	<i>P2</i> ₁ 2 ₁ 2 ₁	<200	0.3	n/a	[9]
K ₄ Mg ₄ (P ₂ O ₇) ₃	<i>Pc</i>	170	1.3	0.0108@1064nm	[18]
Rb ₄ Mg ₄ (P ₂ O ₇) ₃	<i>Amm</i> 2	<200	1.4	0.009@1064nm	[18]
RbNaMgP ₂ O ₇ (LTP)	<i>Pna</i> 2 ₁	185	0.9	0.031@532nm	[47]
RbNaMgP ₂ O ₇ (HTP)	<i>Ccm</i> 2 ₁	185	1.4	0.035@532nm	[47]
K ₂ SrP ₄ O ₁₂	<i>I</i> $\bar{4}$	<200	0.5	0.0160@1064nm	[48]
NaNH ₄ PO ₃ F·H ₂ O	<i>Pn</i>	<176	1.1	>0.053@589.3nm	[18]
(NH ₄) ₂ PO ₃ F	<i>Pna</i> 2 ₁	<177	1	0.027@1064nm	[19]
LiPbPO ₄	<i>Pna</i> 2 ₁	232	3	0.021@1064nm	[15]
Na ₃ Sc ₂ (PO ₄) ₂ F ₃	<i>I4mm</i>	255	0.26	0.0978@546nm	[49]
RbMgPO ₄ ·6H ₂ O	<i>Pmn</i> 2 ₁	288	0.92	0.005@1064nm	[51]
CsMgPO ₄ ·6H ₂ O	<i>P6</i> ₃ <i>mc</i>	258	1.36	0.006@1064nm	[51]
[C(NH ₂) ₃] ₂ HPO ₄ ·H ₂ O	<i>P</i> $\bar{4}$ 2 ₁ <i>c</i>	215	1.2	0.014@532nm	[50]
[C(NH ₂) ₃] ₃ PO ₄ ·2H ₂ O	<i>Pna</i> 2 ₁	250	1.5	0.055@546nm	This work

a) n/a: not reported or not available.

Figure 3 The powder SHG measurements of [C(NH₂)₃]₃PO₄·2H₂O at 1064 nm.

not only in inorganic compounds, but also in organic compounds and metal complexes. According to a detailed discussion by Zyss [53], the anionic group theory can also be applied to calculate the second-order NLO suscept-

ibility of organic molecules, in which the nonlinear optical activating group may be neutral or even positively charged. Therefore, despite the presence of organic cationic groups in the title compound, the calculation method based on the anionic group theory as reported in Ref. [54] was still performed to investigate the structure-optical property relationship. In addition, to better show the relationship between structure and NLO properties, another guanidine phosphate [C(NH₂)₃]₂HPO₄·H₂O (G2HP) [55–56] was employed to compare with the title compound. It will be interesting to compare their SHG contribution of [C(NH₂)₃]⁺ and [PO₄]³⁻ groups by the anionic group theory.

Based on Equations (S2) and (S4) in the Supplementary information, the macroscopic SHG coefficients are mainly depended on the structural criterion *C* and number density of the groups (*n/V*), among which the structural criterion *C* was determined by the arrangement of the groups. It is well-known that the second-order susceptibility of a π -conjugated group is much larger than that of a tetrahedral group. Therefore, for these two

compounds, it can be reasonably inferred that the macroscopic SHG coefficients should mainly depend on the arrangement of $[\text{C}(\text{NH}_2)_3]^+$ groups and the density of $[\text{C}(\text{NH}_2)_3]^+$ groups. In $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$, all $[\text{C}(\text{NH}_2)_3]^+$ cationic groups skew toward the c axis and have the same direction, which is more conducive to the superposition of second-order polarization (Fig. 4a). In

Figure 4 The structure comparison of two guanidine phosphates: (a, c) $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and (b, d) G2HP (the blue plane is guanidine without hydrogen atoms).

contrast, since there is a $\bar{4}$ symmetry axis, the arrangement of $[\text{C}(\text{NH}_2)_3]^+$ cationic groups in G2HP offsets part of the second-order polarization (Fig. 4b). Moreover, the density of $[\text{C}(\text{NH}_2)_3]^+$ groups in the unit cell of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ is larger than that of G2HP. Because the SHG coefficient is proportional to the structural criterion C and the number density of groups (n/V), the calculated values of $C \times (n/V)$ for $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and G2HP are 0.146 and 0.597, respectively. Theoretically, since the calculated value of $C \times (n/V)$ of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ is approximately four times that of G2HP, the SHG response of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ should be much larger than that of G2HP. However, the SHG response of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ is just slightly larger than that of G2HP, which should be attributed to the $[\text{PO}_4]^{3-}$ groups. Unfortunately, in $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$, the polarization direction of the $[\text{PO}_4]^{3-}$ groups is opposite to that of the $[\text{C}(\text{NH}_2)_3]^+$ groups, which offsets the d_{33} contribution from the $[\text{C}(\text{NH}_2)_3]^+$ groups. We can expect that if $[\text{C}(\text{NH}_2)_3]^+$ and $[\text{PO}_4]^{3-}$ are well aligned, the SHG response of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ could be significantly enhanced. Whereas in $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$, although the $[\text{PO}_4]^{3-}$ groups exhibit irregular arrangement in G2HP, they make a positive contribution to d_{14} based on the calculated results. The relevant calculation results are presented in Table 3 and Tables S6, S7.

Theoretical calculations

To further reveal the relationship between the crystal

Table 3 Calculations of anionic group theory and comparison of two guanidinium phosphates

Crystal	Powder SHG intensity	Space group	Structural criterion C of $[\text{C}(\text{NH}_2)_3]^+$	Density of the $[\text{C}(\text{NH}_2)_3]^+$ ($\times 10^{-2} \text{ \AA}^{-3}$)	$C \times (n/V)$ ($10^{-2} \text{ \AA}^{-3}$)	Structural criterion C of $[\text{PO}_4]^{3-}$	Density of the $[\text{PO}_4]^{3-}$ (n/V) ($\times 10^{-2} \text{ \AA}^{-3}$)	$C \times (n/V)$ ($10^{-2} \text{ \AA}^{-3}$)
$[\text{C}(\text{NH}_2)_3]_3\text{HPO}_4 \cdot \text{H}_2\text{O}$	$1.2 \times \text{KDP}$	$P\bar{4}2_1c$	0.214	0.681	0.146	0.399	0.389	0.155
$[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$	$1.5 \times \text{KDP}$	$Pna2_1$	0.743	0.803	0.597	0.994	0.268	0.194

Figure 5 Electronic properties of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$: (a) band structure; (b) total and partial DOS.

structure and optical properties, the electronic bands of the title compound were simulated based on first-principles calculations. The calculated band structure is presented in Fig. 5a, showing a direct band gap of 3.68 eV for the title compound. The predicted energy band gap was slightly smaller than the experimental value (4.20 eV) and the scissor operator was applied to shift all conduction bands upward.

Since the optical properties mainly depend on the states close to the Fermi level, only the upper region of the valence band (VB) and the bottom of the conduction band (CB) were analyzed. The total and partial densities of states (DOS and PDOS) for the title compound are shown in Fig. 5b. At the top of the VB, the band is mostly composed of O-2p, P-3p, and N-2p orbitals. The bottom of CB is predominately derived from C-2p, N-2p, and H-1s orbitals. From the PDOS calculations, it could be concluded that the linear and nonlinear optical properties of the title compound are primarily due to the synergistic effect of π -conjugated trigonal planar $[\text{C}(\text{NH}_2)_3]^+$ groups and $[\text{PO}_4]^{3-}$ tetrahedra.

The calculated refractive index curves of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ were also obtained. Since the calculated refractive index curves have the tendency of $n_c > n_b > n_a$ in the wavelength of 300–2000 nm, the birefringence can be calculated by $\Delta n = n_c - n_a$, where n_a , n_b , and n_c represent the refractive indices in the a , b , and c directions. As shown in Fig. S6, $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ has relatively large birefringences of 0.053@546.1 nm and 0.05@1064 nm, which are close to the experimental results. It is well known that large birefringence in phosphate will promote the shortest PM wavelength blue shift to a shorter region. According to the calculated refractive index dispersion curve, the shortest PM wavelength was estimated to be 318 nm (Fig. S7).

The SHG coefficients d_{ij} were calculated by using the formula developed by Lin *et al.* [57,58]. Under the restriction of Kleinman's symmetry [59], the $Pna2_1$ space group of the title compound leads to three non-zero independent SHG coefficients: $d_{15} = -0.31 \text{ pm V}^{-1}$, $d_{24} = -0.49 \text{ pm V}^{-1}$, and $d_{33} = 0.84 \text{ pm V}^{-1}$, respectively (Fig. S8). The largest calculated SHG tensor d_{33} is approximately twice that of KDP ($d_{36} = 0.39 \text{ pm V}^{-1}$), which is basically in accordance with the experimental result. To investigate the contribution of the SHG response, the SHG-densities of occupied and unoccupied states were calculated as shown in Fig. S9. In the occupied states, the SHG densities are mainly accumulated on N and O. While in the unoccupied states, the C atoms and N atoms are dominant. Therefore, the SHG effect of $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ may come from the synergistic effects of the C–N and P–O groups.

$[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ may come from the synergistic effects of the C–N and P–O groups.

CONCLUSIONS

In conclusion, we successfully synthesized a new metal-free UV NLO phosphate, $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$, via a simple solution evaporation method. Notably, $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ achieved a subtle balance with remarkable SHG effect ($1.5 \times \text{KDP}$), enlarged birefringence (0.055@546 nm), and short UV cut-off edge (250 nm), indicating that $[\text{C}(\text{NH}_2)_3]_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ should be a promising UV NLO crystal. Theoretical calculations indicate that its superior optical properties mainly originate from the π -conjugated trigonal planar $[\text{C}(\text{NH}_2)_3]^+$ and $[\text{PO}_4]^{3-}$. This study shows that the introduction of organic π -conjugated $[\text{C}(\text{NH}_2)_3]^+$ cations into phosphates will be an effective strategy for obtaining UV NLO phosphates with large birefringence and SHG.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper. Accession Codes: CCDC 2036309 contain the supplementary crystallographic data for this paper.

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[C(NH₂)₃]₃PO₄·2H₂O: 一种具有大双折射和大倍频响应的新型无金属紫外磷酸盐非线性光学晶体

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摘要 [PO₄]³⁻具有较小的微观二阶极化率和极化各向异性, 这往往导致磷酸盐具有较小的倍频效应和双折射率。本文采用溶液蒸发法设计并合成了新型非中心对称磷酸盐[C(NH₂)₃]₃PO₄·2H₂O。无金属离子的[C(NH₂)₃]₃PO₄·2H₂O由平面共轭胍阳离子和磷酸根四面体组成, 并通过氢键连接形成三维网络。物理性能测量表明, 与大多数报道的紫外非线性光学材料中的磷酸盐相比, 标题化合物显示出更大的双折射(0.055@546.1 nm)和大倍频响应(1.5 × KDP)。此外, 第一性原理计算表明, π共轭的平面[C(NH₂)₃]⁺阳离子和[PO₄]³⁻基团是其优异的线性和非线性光学特性的来源。