

π -Conjugated Trigonal Planar $[\text{C}(\text{NH}_2)_3]^+$ Cationic Group: A Superior Functional Unit for Ultraviolet Nonlinear Optical Materials

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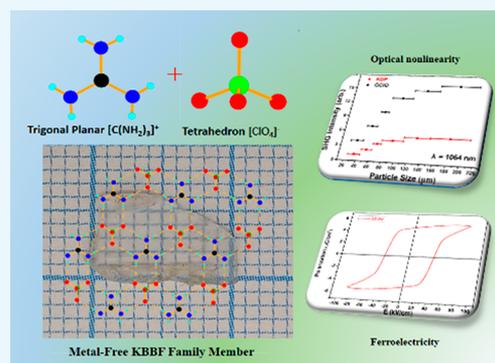
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ABSTRACT: Employing π -conjugated anionic groups in molecular construction has been proven to be an effective strategy to find superior ultraviolet (UV) nonlinear optical (NLO) crystals over the decades. Herein, unlike the traditional π -conjugated anionic groups, we identify that a π -conjugated cationic group, viz., $[\text{C}(\text{NH}_2)_3]^+$, is also an excellent UV NLO-active functional group in theory. Furthermore, we identify a $[\text{C}(\text{NH}_2)_3]^+$ -containing compound, $\text{C}(\text{NH}_2)_3\text{ClO}_4$, as a promising UV NLO candidate due to its short UV cutoff edge (200 nm), remarkable second-harmonic generation effect ($\sim 3 \times \text{KDP}$), and moderate birefringence of $0.076@1064 \text{ nm}$. Additionally, $\text{C}(\text{NH}_2)_3\text{ClO}_4$ has excellent ferroelectric properties and reversal of domains, which also enables it to produce ultraviolet coherent light as short as 200 nm by a quasi-phase matching technique with a periodically poling method. Our study may provide not only a promising UV NLO crystal but also a new π -conjugated functional unit, $[\text{C}(\text{NH}_2)_3]^+$, which will open a path to finding new classes of high-performance UV NLO crystals.



INTRODUCTION

Ultraviolet (UV) nonlinear optical (NLO) crystals, especially which can produce high-power coherent light in the solar-blind (210–280 nm) region, are increasingly required for numerous applications in military confrontation, precise diagnosis, semiconductor manufacturing, and laser micromatching.^{1–3} However, high-performance UV NLO materials are still lacking due to the extremely rigorous prerequisites, including strong second-harmonic generation (SHG) coefficients ($d_{ij} > 1 \text{ pm/V}$), wide transparency range (down to $\sim 200 \text{ nm}$), and large birefringence.⁴ By now, only a small amount of NLO crystals can be used in the solar-blind region. Notably, among them, the materials with fabulous NLO performance, such as $\beta\text{-BaB}_2\text{O}_4$ (BBO),⁵ $\text{CsLiB}_6\text{O}_{10}$ (CLBO),⁶ ABCO_3F ($A = \text{K}$ and Rb ; $B = \text{Mg}$, Ca , and Sr),⁷ and $\text{Re}(\text{NO}_3)\text{OH}$ ($\text{Re} = \text{La}$, Y , and Gd),⁸ all have trigonal planar π -conjugated anionic groups including $(\text{BO}_3)^{3-}$, $(\text{CO}_3)^{2-}$, and $(\text{NO}_3)^-$ groups. These anionic groups have the following merits: (1) a large optical bandgap mainly attributed from the electronegativity difference between the constituent atoms, which is in favor of UV transparency; (2) strong anisotropic polarizability due to their planar configuration, which is in favor of phase matching; (3) high second-order hyperpolarizability (χ^2) due to their delocalized π orbitals, which is favorable for producing large macroscopic SHG response. These merits make them very suitable for constructing UV NLO crystals. Therefore, expanding the study on the trigonal planar π -conjugated group is instrumental in developing new UV NLO materials.

To date, inorganic trigonal planar groups systems, including borates, carbonates, and nitrates, have been extensively

investigated.^{9–19} Besides these three systems, to our knowledge, no other inorganic trigonal π -conjugated group is favorable for developing UV NLO crystals. In recent years, metal cyanurates have attracted wide attention because the structure geometry of the organic $(\text{C}_3\text{N}_3\text{O}_3)^{3-}$ group is very similar to the inorganic $(\text{B}_3\text{O}_6)^{3-}$ group. Very recently, our group further confirmed that hydro-isocyanurate $(\text{HC}_3\text{N}_3\text{O}_3)^{2-}$ and dihydro-isocyanurates $(\text{H}_2\text{C}_3\text{N}_3\text{O}_3)^-$ are excellent units for developing UV NLO crystals as well.^{20,21} Inspired by the development of cyanurate systems, we have been searching for trigonal planar groups among organic groups. As a result, a $[\text{C}(\text{NH}_2)_3]^+$ group has been screened out based on first-principles theoretical studies.

The $[\text{C}(\text{NH}_2)_3]^+$ group is cationic, different from traditional trigonal planar π -conjugated anionic groups. Calculation results of the $[\text{C}(\text{NH}_2)_3]^+$ cationic group, including dipole moment, anisotropy polarizability, hyperpolarizability, and HOMO–LUMO gap, were compared with those of $(\text{BO}_3)^{3-}$, $(\text{CO}_3)^{2-}$, and $(\text{NO}_3)^-$ groups as presented in Figure 1. As can be seen from Figure 1, the $[\text{C}(\text{NH}_2)_3]^+$ cationic group has the largest optical gap of 8.53 eV (corresponding to an absorption edge of 143 nm) as well as the highest striking anisotropy

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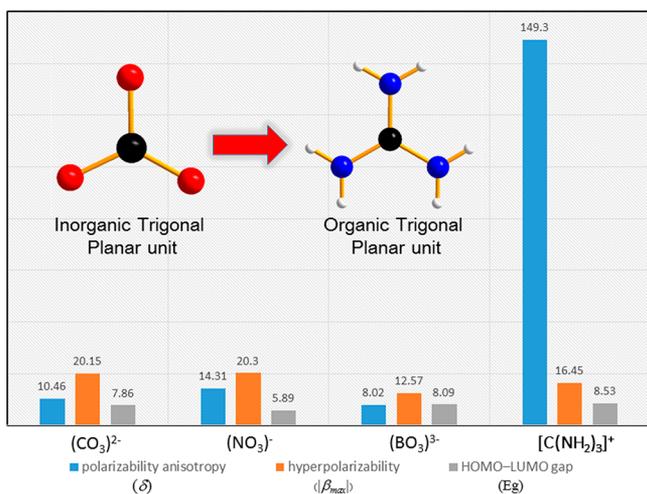


Figure 1. Calculation results of $(CO_3)^{2-}$, $(NO_3)^-$, $(BO_3)^{3-}$, and $[C(NH_2)_3]^+$ groups.

polarizability of 149.3 (more than ten times higher than those of the other three anionic groups). In addition, the $[C(NH_2)_3]^+$ cationic group presents a large hyperpolarizability, which is comparable to those of $(CO_3)^{2-}$ and $(NO_3)^-$ groups and larger than that of the $(BO_3)^{3-}$ group. Thus, we predicted that the trigonal planar π -conjugated $[C(NH_2)_3]^+$ cationic group is a superior materials gene for developing UV NLO crystals.

To verify our predictions, we first systematically searched the noncentrosymmetrical $[C(NH_2)_3]^+$ -based compounds. As a result, metal-free $C(NH_2)_3ClO_4$ (GCIO) was screened out because it has a similar layer with that of KBBF. We further experimentally prepared GCIO and showed that the growth of bulk crystals is feasible. As expected, since GCIO has a similar topological layered structure to KBBF, it possesses excellent

optical properties including a short UV cutoff edge of 200 nm, a strong SHG effect of about 3 times that of KH_2PO_4 (KDP), and sufficient birefringence. More importantly, GCIO is a unity of optical nonlinearity and ferroelectricity; thus, it also can be used as a quasi-phase matching UV NLO crystal.

RESULTS AND DISCUSSION

GCIO crystallizes in the acentric trigonal space group $R3m$ with lattice parameters $a = b = 7.605 \text{ \AA}$, $c = 9.121 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$, which is in accordance with previous reports.^{22–24} Though GCIO is a known compound, either the comprehensive study of its UV NLO properties or its insightful structure feature has been overlooked. In its asymmetric unit, there is one independent C, N, H, Cl, and O atom. All C atoms are coordinated to three nitrogen atoms forming a trigonal-planar coordination $C(NH_2)_3^+$ group with the C–N bond length of 1.357(12) \AA . These isolated planar $C(NH_2)_3^+$ groups aligned parallel in the a – b plane, which are responsible for the strong SHG effect and large birefringence. Also, all Cl atoms are surrounded by four oxygen atoms forming ClO_4^- tetrahedra with the Cl–O bond lengths of 1.428(3) \AA , which connect with $C(NH_2)_3^+$ groups through the interionic N–H \cdots O hydrogen bonds to form 2D $[C(NH_2)_3ClO_4]_\infty$ layers (Figure 2). It shall be noted that 2D $[C(NH_2)_3ClO_4]_\infty$ layers in GCIO are roughly similar to the 2D $[Be_2BO_3F_2]_\infty$ layers in KBBF, but there is also a difference between them. The similarity lies in that GCIO inherits the ideal structure features of KBBF, namely, all the parallel $[C(NH_2)_3]^+$ planar triangle units align them along the same direction within a layer, which is favorable for a large macroscopic SHG effect and strong optical anisotropy. The difference is that GCIO improves the deficiency of the $[Be_2BO_3F_2]_\infty$ layer of KBBF. Specifically, the alternant $[BeO_3F]$ tetrahedral groups within the $[Be_2BO_3F_2]_\infty$ layer of KBBF are aligned in the opposite direction, resulting in no contribution to NLO coefficients,

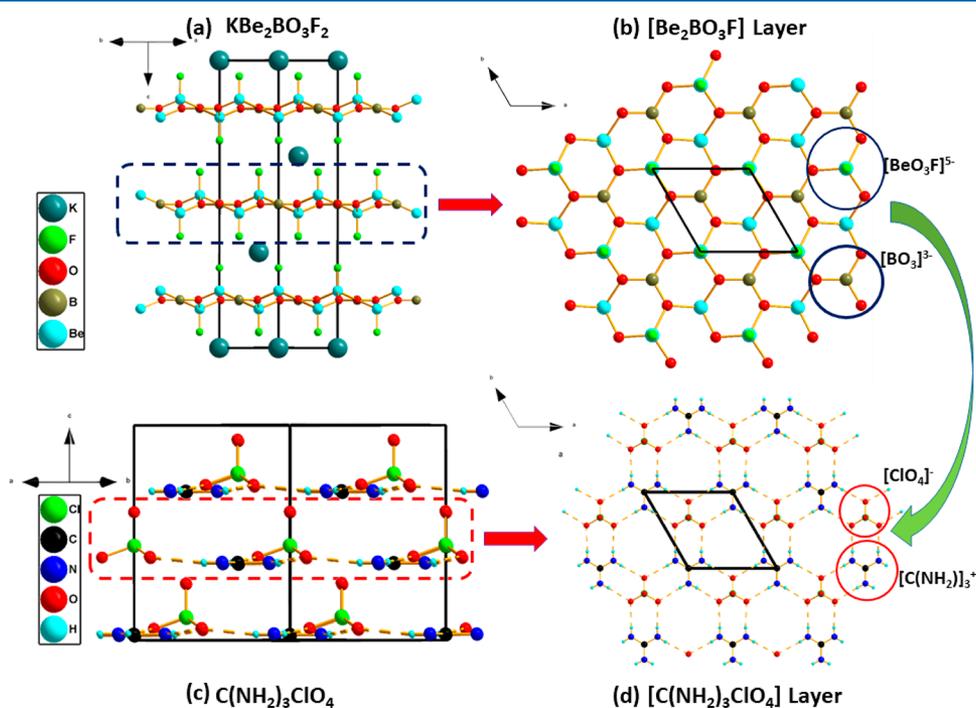


Figure 2. Structural evolution from KBBF to GCIO: (a) structure of KBBF, (b) $[Be_2BO_3F]_\infty$ layer in KBBF, (c) structure of GCIO, and (d) $[C(NH_2)_3ClO_4]_\infty$ layer in GCIO.

while all $[\text{ClO}_4]$ tetrahedral groups within the $[\text{C}(\text{NH}_2)_3\text{ClO}_4]_\infty$ layer of GClO are oriented in the same direction, which is beneficial for achieving additional SHG enhancement.

Thermal stability of GClO was examined by thermogravimetric (TG) and differential thermal analyses (DTA) (Figure S2). In the differential thermogram, there is one exothermic peak at $\sim 180^\circ\text{C}$, which can be assigned to the phase transition point according to the previous reports.²⁵ In addition, as there is no weight loss before 280°C , the material is moisture-free and stable up to 280°C .

The transmittance spectrum measurement on a crystal wafer with a size of $20 \times 10 \times 1 \text{ mm}^3$ (Figure 3b) reveals that GClO has a short UV cutoff edge of 200 nm (Figure 3a), which basically meets the application requirement of the UV region.

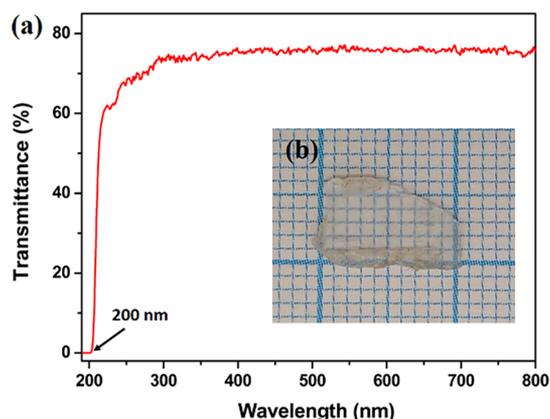


Figure 3. (a) Transmission spectrum of GClO. (b) Crystal photograph of GClO with a size of $20 \times 10 \times 1 \text{ mm}^3$.

The powder SHG signal of GClO was tested using the Kurtz–Perry method,²⁶ which revealed that its SHG intensity is about 3 times that of KDP at 1064 nm as well as it is phase-matchable (Figure 4a). Furthermore, applying Kleinmann symmetry in a 3 m point group, we calculated three nonzero and independent SHG coefficients of GClO ($d_{11} = 1.50 \text{ pm/V}$, $d_{31} = -0.56 \text{ pm/V}$, and $d_{33} = 0.87 \text{ pm/V}$), where the largest SHG coefficient d_{11} is about three times that of KDP ($d_{36} = 0.39 \text{ pm/V}$) that is in accordance with the experimental ones. Notably, this remarkable SHG efficiency is nearly triple that of KBBF ($\sim 1.2 \times \text{KDP}$) and is comparable to those of some metal-containing KBBF family members, such as $\text{Rb}_3\text{Al}_3\text{B}_3\text{O}_{10}\text{F}$ ($1.2 \times \text{KDP}$), $\text{Cs}_3\text{Zn}_6\text{B}_9\text{O}_{21}$ ($3.3 \times \text{KDP}$), $\text{AZn}_2\text{BO}_3\text{X}_2$ ($A = \text{Na, K, Rb, and NH}_4; X = \text{Cl and Br}$) ($2.5\text{--}3.01 \times \text{KDP}$), and $\text{Zn}_2\text{BO}_3\text{OH}$ ($\sim 1.5 \times \text{KDP}$).^{15,27–29} It is well-known that in terms of KBBF-type compounds, their SHG contribution mainly stems from their coparallel planar $(\text{BO}_3)^{3-}$ triangles units. Accordingly for GClO, the uniform alignment of planar $[\text{C}(\text{NH}_2)_3]^+$ triangle units should mainly be responsible for its SHG coefficients. To confirm the SHG contribution from the planar cationic $[\text{C}(\text{NH}_2)_3]^+$ group, SHG-weighted electron density analysis was adopted. The SHG process includes two virtual transition processes, namely, virtual electron (VE) and virtual hole (VH) processes. Since the VE process is dominant in the SHG process, the largest SHG tensor (d_{11}) in the VE process is analyzed, and the results are presented in Figure 4c,d. The contributions of occupied states to d_{11} are mostly derived from the nonbonding 2p orbitals of nitrogen and oxygen atoms, while the contributions of unoccupied states are mainly determined by the anti π orbitals of the $[\text{C}(\text{NH}_2)_3]^+$ groups. The calculated results revealed that the $[\text{C}(\text{NH}_2)_3]^+$ groups play key roles in the SHG response.

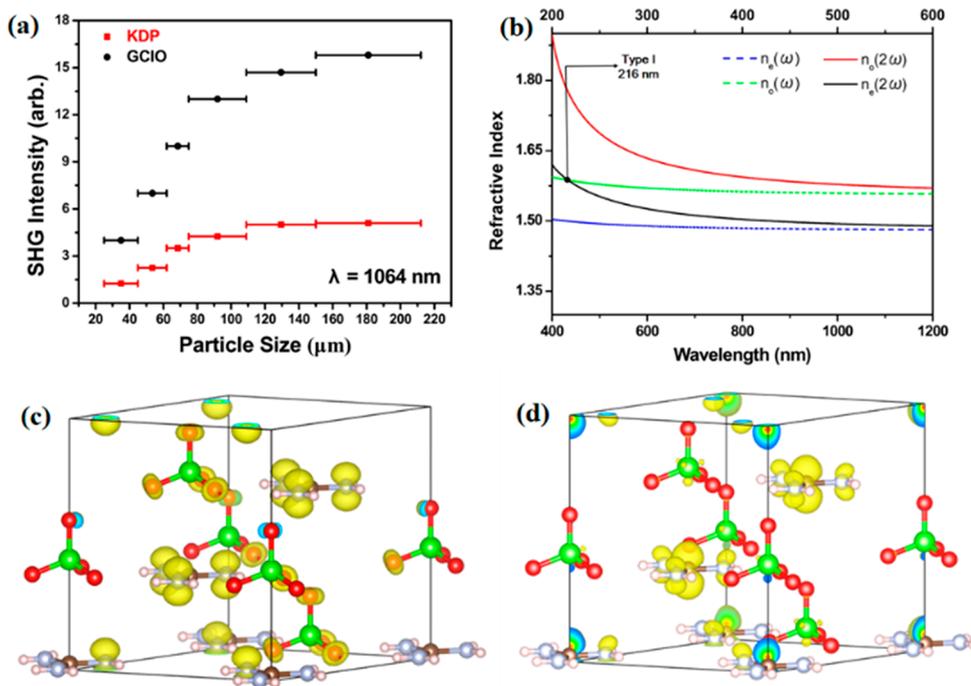


Figure 4. (a) Powder SHG measurements at 1064 nm. (b) Calculated type I phase matching condition of GClO. Dashed lines: refractive indices of fundamental light. Solid lines: refractive indices of second-harmonic light. SHG-weighted electron density maps of occupied (c) and unoccupied (d) states in the VE process of d_{11} .

Birefringence (Δn) is a key performance indicator for practical UV NLO crystals because it directly determines the phase matching ability of crystals. The calculated birefringence indicates that GClO has a moderate birefringence of $0.076@1064$ nm, which can be comparable to KBBF ($0.07@1064$ nm). Based on the relationship between the structure and properties of KBBF-type compounds, one can deduce that the moderate birefringence of GClO should originate from a coplanar configuration of $[\text{C}(\text{NH}_2)_3]^+$ groups. Furthermore, according to the calculated dispersion of the refractive indices, we could estimate the phase matching (PM) ability of GClO. Employing the method reported in ref 30, the refractive index dispersion curves of fundamental (dashed lines) and second-harmonic (solid lines) light for GClO are plotted in Figure 4b. According to the birefringence PM conditions, type I PM can occur when $n_o(\omega)$ is equal to $n_e(2\omega)$. Therefore, the shortest type I PM SHG wavelength occurs at 216 nm, where the green dashed line crosses the black solid line. It indicates that GClO may be used for direct fourth-harmonic generation at 266 nm from an Nd:YAG laser.

In addition, it is noteworthy that the single crystal of GClO shows good polarization/current–electric field hysteresis loops (Figure 5), which confirms its excellent ferroelectric polar-

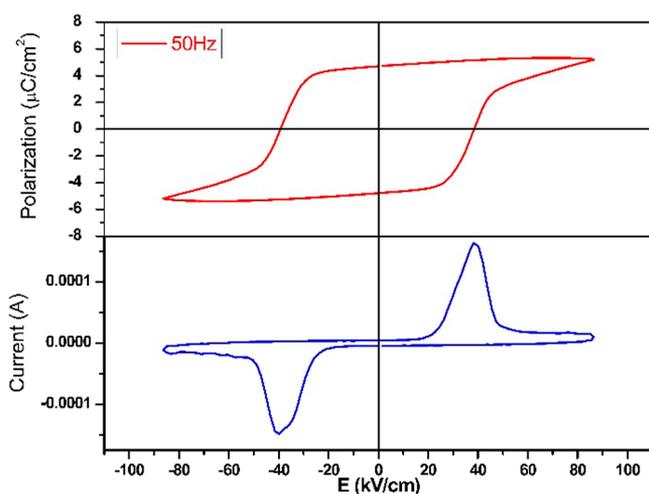


Figure 5. Polarization/current–electric field hysteresis loops at 298 K. The absolute polarization reversal appears at a coercive field of 38.51 kV cm^{-1} and a remanent polarization of $4.74 \mu\text{C cm}^{-2}$ at the frequency of 50 Hz.

ization reversal characteristic. Thus, a unity of optical nonlinearity and ferroelectricity in GClO makes it also capable of being a quite rare periodically poled crystal that may be applied in the UV region.³¹ As a quasi-phase crystal, the shortest frequency conversion wavelength will reach its absorption edge (~ 200 nm) without the limitation of a birefringence, and it could get the utmost out of the largest nonlinear coefficient (d_{11}) due to the unrestricted phase matching directions. In addition, as the length of the crystal increases, the conversion efficiency can increase without any walk-off effect.

Reagents and Synthesis. Guanidine carbonate (99.8%) and HClO_4 (70–72%) were purchased from Adamas without further purification. Guanidine carbonate (5.4 g) and HClO_4 (10 mL) were used. After about several hours, colorless plate-like crystals were obtained.

Growth of Crystals. Crystals of GClO were grown by a water solution method. Raw material GClO (200 g) was dissolved in H_2O (100.0 mL). The mixture was evaporated in an incubator at 35°C for several weeks. Colorless bulk crystals of GClO were obtained.

Single-Crystal Structure Determination. Single-crystal X-ray diffraction data of GClO were obtained on a Bruker Smart APEX II CCD equipped with graphite-monochromatic $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The operating temperature is 293 K. The structure was solved and refined by using SHELXL-97.³² Furthermore, the structure was confirmed by using the ADDSYM algorithm from the program PLATON.³³ The details of the crystallographic data and structure refinement information for $\text{C}(\text{NH}_2)_3\text{ClO}_4$ are listed in Table S1. Atomic coordinates and isotropic displacement coefficients are listed in Table S2, and bond lengths and angles ($^\circ$) are listed in Table S3.

Powder X-ray Diffraction. X-ray diffraction patterns of polycrystalline materials were obtained on a Miniflex600 powder X-ray diffractometer by using $\text{Cu K}\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$) at room temperature in the angular range of $2\theta = 5\text{--}75^\circ$ with a scan step width of 0.05° and a fixed time of 0.2 s. The powder XRD pattern of $\text{C}(\text{NH}_2)_3\text{ClO}_4$ was in accordance with the calculated one based on the single-crystal model, showing that the phase is pure (Figure S1).

Thermal Analysis. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were performed on a NETZCH STA 449F3. The measured temperature range on the reference (Al_2O_3) and crystal samples was $30\text{--}1100^\circ\text{C}$, and the heating rate was 10°C/min under a constant flow of nitrogen gas.

UV–Vis Transmittance Spectroscopy. The UV–vis transmittance ranging from 190 to 800 nm of GClO was collected on a PerkinElmer Lambda-950 UV/vis/NIR spectrophotometer at room temperature.

Second-Harmonic Generation. Powder SHG efficiencies of polycrystalline GClO were studied via a modified Kurtz and Perry method. The GClO and reference KDP samples were ground and sieved into the following particle size ranges: 25–45, 45–62, 62–75, 75–109, 109–150, and 150–212 μm , which were measured by using a Q-switched Nd:YAG laser at 1064 nm.

Ferroelectric Properties. The ferroelectric properties were examined by an aix-ACCT TF Analyzer 2000 ferroelectric test system, a computer-controlled Alpha-A broadband dielectric/impedance spectrometer (NovoControl, GmbH), and a polarized light microscope (LV100POL, Nikon, Japan) with ferroelectric hysteresis loops and ferroelectric domains.

Computational Descriptions. First-principles calculations were performed by a CASTEP package based on density functional theory (DFT).^{26,34} The valence electrons of component elements were $\text{C } 2s^22p^2$, $\text{N } 2s^22p^3$, $\text{O } 2s^22p^4$, and $\text{Cl } 3s^23p^5$. Generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE)^{35,36} was selected to describe the exchange and correlative potential of electron–electron interactions. A Monkhorst–Pack scheme³⁷ k -mesh density of $2 \times 2 \times 2$ was used in the first Brillouin zone of the unit cell. Energy cutoff and converge criteria were all set to be 750 eV. The self-consistent convergence of the total energy was 1.0×10^{-5} eV/atom. The SHG coefficients were calculated by using the “velocity-gauge” formula derived by Sipe et al.^{38,39} Also, the SHG density of d_{11} was studied by a band-resolved method.^{40,41} The electronic structures of $(\text{BO}_3)^{3-}$, $(\text{CO}_3)^{2-}$,

(NO₃)⁻, and [C(NH₂)₃]⁺ groups in the molecular level were obtained using the DFT method implemented by the Gaussian 09 package at the 6-31G level.

CONCLUSIONS

In summary, our theoretical calculations revealed that the trigonal planar [C(NH₂)₃]⁺ cationic group exhibits superior linear and nonlinear optical properties compared with those of inorganic trigonal planar anionic groups including BO₃, NO₃, and CO₃. In addition, a metal-free KBBF member, C-(NH₂)₃ClO₄, was screened out, and bulk crystals were successfully grown using the solution method. It has a similar topological layer with KBBF and shows a short UV cutoff edge (200 nm) as well as remarkable SHG efficiency (3.0 × KDP at 1064 nm). The calculations revealed that the shortest SHG phase matching wavelength of C(NH₂)₃ClO₄ is about 216 nm by a direct birefringence phase matching technique. In addition, a unity of optical nonlinearity and ferroelectricity also makes it a quite attractive material for generating UV coherent light as short as 200 nm by means of the quasi-phase matching technique. Our study results show that [C(NH₂)₃]⁺-based compounds will be good candidates for UV NLO crystals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c00736>.

Details of additional figures and tables (X-ray powder diffraction patterns, TGA and DTA curves, and calculated bandgap of (NH₂)₃ClO₄; crystal data and structure refinement for C(NH₂)₃SO₃F, atomic coordinates and equivalent isotropic displacement parameters, and bond lengths and angles for C(NH₂)₃ClO₄) (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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