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Na₃B₆O₁₀(HCOO): an ultraviolet nonlinear optical sodium borate-formate†

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A new sodium borate-formate, Na₃B₆O₁₀(HCOO) (**1**), has been successfully synthesized in a surfactant-thermal system. Compound **1** crystallizes in the orthorhombic system, with the polar *P2₁2₁2₁* space group and the parameters *a* = 7.6375(8) Å, *b* = 9.9345(9) Å, *c* = 12.7231(13) Å, *V* = 965.36(17) Å³, and *Z* = 4. Compound **1** contains basic building units of (B₆O₁₃)⁸⁻, and each (B₆O₁₃)⁸⁻ unit connects with six other neighboring units and forms a novel 3D open-framework with 9R channels. The channels accommodate Na⁺ ions and HCOO⁻ units. The whole framework can be simplified as a *pcu*-type net. Compound **1** shows a moderate second-harmonic-generation (SHG) signal, a short cut-off edge in the ultraviolet (UV) region, and a suitable birefringence of 0.062 at 1064 nm. These characteristics reveal that compound **1** is a promising UV nonlinear optical crystal. Density functional theory calculations show that the B–O and HCOO⁻ units are responsible for the nonlinear optical properties of **1**.

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Introduction

Ultraviolet (UV) and deep-UV nonlinear optical (NLO) materials can generate coherent UV and deep UV light through solid-state lasers, and are widely used in photolithography and semiconductor manufacturing.^{1–10} In a comprehensive viewpoint, Halasyamani and co-workers summarized the features of a perfect UV and deep-UV NLO material: a wide transparency region, large second-harmonic generation (SHG) coefficients, moderate birefringence, large laser damage threshold, chemical stability, and easy growth of large high-quality single crystals.¹¹ Alkali- and alkaline-earth-metal borates are important sources of UV NLO materials. β-BaB₂O₄ (BBO), LiB₃O₅ (LBO), and CsLiB₆O₁₀ (CLBO) are commercial products, and are known as excellent UV NLO materials.¹² The combination of borates with other selected anions in one acentric structure may improve their NLO properties. In KBe₂BO₃F₂ (KBBF) containing [(BeO₃F)(BO₃)] layers and separated K⁺ ions, blue-shifted cutoff edges have been observed due to the high electronegativity of fluorine ions, and KBBF can generate

coherent deep-UV radiation at 177.3 nm through frequency conversion.¹³ The groups of Pan and Ye further developed the fluorooxoborate system,^{14,15} where NH₄B₄O₆F is impressive with an enhanced SHG efficiency (2.5KBBF). NH₄B₄O₆F does not contain toxic beryllium ions and bulk crystals can be easily grown.^{14a}

CO₃²⁻ shows a similar planar triangle structure to BO₃³⁻, and the incorporation of CO₃²⁻ into borates gives a new family of borate-carbonates.¹⁶ NaRb₃B₆O₉(OH)₃(HCO₃) contains isolated HCO₃⁻ groups and [B₆O₉(OH)₃]³⁻ chains and exhibits a transparency of about 40% at 200 nm and a moderate SHG response (0.5KDP).¹⁷ Borate-iodates are also known,¹⁸ with Be₂(BO₃)(IO₃) featuring a typical KBBF structure, in which honeycomb Be₂BO₅ layers are linked by IO₃⁻ groups, and shows a large birefringence (Δ*n* = 0.172) and a very strong SHG response (7.2KDP) due to the introduction of trigonal-pyramidal IO₃⁻ anions.^{18a} The introduction of tetrahedral SiO₄⁴⁻, GeO₄⁴⁻, and PO₄³⁻ groups is also reported.^{19–21} For example, Cs₂GeB₄O₉ consisting of corner-sharing B₄O₉ and GeO₄ tetrahedra, is a new UV NLO crystal with a strong SHG response (2.8KDP) and large crystal dimensions of about 20 × 16 × 8 mm³ grown by a high-temperature top-seeded solution method.^{20a} In addition, with judicious selection of stereochemically active lone pair cations, a stronger SHG response is possible. Bi₃TeBO₉ (20KDP), Pb₂B₅O₉I (13.5KDP), Pb₂BO₃I (10KDP), and Pb₂(BO₃)(NO₃) (9KDP) are notable examples,^{22–25} in which Pb₂BO₃I has the highest SHG response in the KBBF family. However, these NLO crystals are not suitable for use in the UV and deep-UV regions due to their red-shifted absorption edges.²⁴

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Alkali- and alkaline-earth-metal formates are known as UV NLO crystals. For example, the output of UV light at around 243 nm with 1.4 mW of power has been achieved using frequency conversion with a HCOOLi-H₂O single crystal, and a theoretical calculation further indicates that HCOO⁻ dominates the contribution to the SHG efficiency.^{26,27} Recently, Huang, Zou, and co-workers investigated the borate-formate system, and synthesized Na(HCOO)(H₃BO₃)(H₂O)₂, (HCOOH)₃(H₃BO₃)₂·3H₂O, and M₃(HCOO)₃(H₃BO₃)₂ (M = K, Rb, Cs, NH₄).^{28,29} (NH₄)₃(HCOO)₃(H₃BO₃)₂ shows graphite-like layers *via* the linkage of hydrogen bonding, and this compound is a UV NLO crystal with a large birefringence of 0.156 at 546 nm.²⁹ Note that all of these borate-formates contain isolated H₃BO₃ molecules, and short UV absorption edges are found in these compounds. It is interesting to continue synthesizing UV NLO materials in the borate-formate system; other crystalline phases with different polyborate anions may be obtained.

In recent years, we obtained a new family of UV and deep-UV NLO alkali- and alkaline-earth-metal borates,^{30–32} including LiBa₃(OH)[B₉O₁₆][B(OH)₄], Li₂CsB₇O₁₀(OH)₄, and Ba₂B₁₀O₁₆(OH)₂·(H₃BO₃)(H₂O). Ba₂B₁₀O₁₆(OH)₂·(H₃BO₃)(H₂O) exhibits a layered structure with two different boron oxide units of H₃BO₃ mole-

cules and [B₅O₁₀(OH)]⁶⁻ anions, and this barium borate is a possible deep-UV nonlinear-optical material.³² In this work, we obtained a new sodium borate-formate, Na₃B₆O₁₀(HCOO) (1), which contains both borate and formate anionic groups, and displays a 3D open-framework structure with a primitive cubic net. Compound 1 is a potential UV NLO crystal owing to its moderate SHG signal intensity, short UV cutoff edge, and suitable birefringence of 0.062 at 1064 nm.

Methods

Calculation method

The electronic band structure of 1 was calculated by the local density approximation (LDA) combined with the pseudopotential plane wave method implemented in the CASTEP code of Material Studio 4.0.³³ The cutoff energy of the plane wave base was set to 750 eV. The Monkhorst-Pack *k*-point sampling was set to the *k*-point separation of 0.005 Å⁻¹ (equivalent to 26 × 20 × 16) and 0.015 Å⁻¹ for calculating the electronic band structure and the density of states, respectively. The optical properties of 1 were determined using the sum-over-states (SOS) method implemented in our SOS program.^{34,35} The

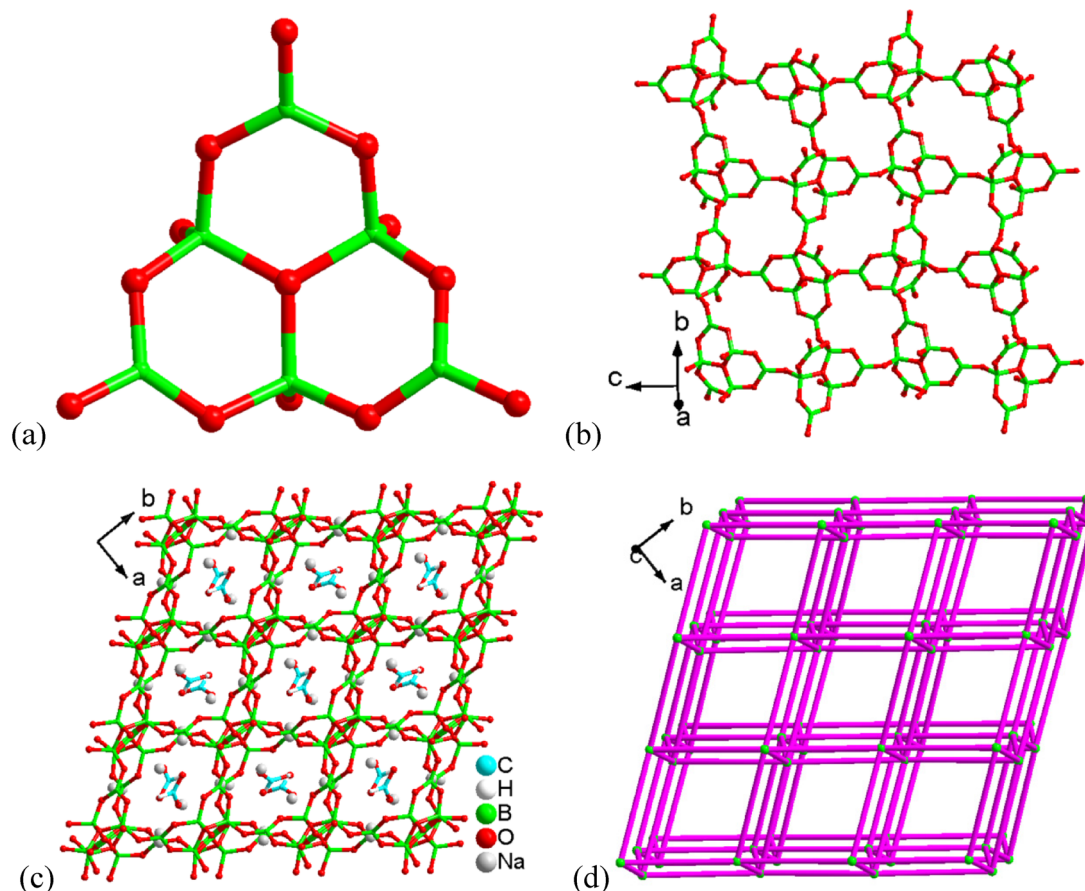


Fig. 1 (a) (B₆O₁₃)⁸⁻ cluster in 1. (b) View of the layer in 1 along the *a*-axis. (c) Framework structure of 1 viewed along the *c*-axis, with Na⁺ and HCOO⁻ ions occupying the channels. (d) The simplified pcu-type net in 1, in which the (B₆O₁₃)⁸⁻ clusters are shown as green nodes.

Monkhorst–Pack k -point sampling of 0.01 \AA^{-1} (equivalent to $13 \times 10 \times 8$) and 200 empty bands were used in the SOS calculations.

Experimental method

Synthesis of **1**. A mixture of HCOONa (1 mmol, 0.068 g), 0.25 mL NaOH (4 mol L^{-1}), 333 μL trimethyl borate, 1 mL formamide and 4 mL PEG-400 was sealed in a 30 mL Teflon-lined bomb at $180 \text{ }^\circ\text{C}$ for 6 days, and then cooled to room temperature. Colorless lamellar crystals of **1** were obtained by filtration, which were washed with distilled water, and dried in air (15% yield based on HCOO^-). IR (KBr, cm^{-1}): 3433(s), 2974(w), 2779(w), 2697(m), 1626(s), 1349(s), 1172(m), 1072(w), 1022(s), 902(w), 851(w), 744(w), 694(w), 625(w), 599(w), 524(w) (Fig. S1†).

Results and discussion

Colorless crystals of **1** were synthesized through surfactant-thermal reactions of HCOONa, NaOH, trimethyl borate, and formamide in poly(ethylene glycol)-400 at $180 \text{ }^\circ\text{C}$ for 6 days (see the Experimental section). It should be stressed that compound **1** could not be obtained when inorganic H_3BO_3 was used as the B source under similar conditions. The powder

X-ray diffraction (PXRD) patterns indicate the phase purity of **1** (Fig. S2†). Compound **1** crystallizes in the orthorhombic polar space group $P2_12_12_1$ (Table S1†).³⁶ In the asymmetric unit of **1**, there are one unique B_6O_{10} unit, one unique HCOO^- , and three Na ions (Fig. S3†). The calculated bond-valence-sums of B, Na, and O atoms are consistent with their valences of $3+$, $1+$, and $2-$, respectively. The B atoms show two coordination modes of BO_4 tetrahedra (B2, B3, B5) and BO_3 triangles (B1, B4, B6). The basic building unit of $(\text{B}_6\text{O}_{13})^{8-}$ contains three 3-rings (3R), and consist of three BO_4 tetrahedra (T) and three BO_3 triangles (Δ), which are connected by corner-sharing oxygen atoms (Fig. 1a). The symbol of the $(\text{B}_6\text{O}_{13})^{8-}$ unit can be written as $(6 : 3\Delta + 3T)$. The B–O bond distances vary from 1.349(4) to 1.378(4) \AA for the BO_3 triangles and from 1.429(4) to 1.529(3) \AA for the BO_4 tetrahedra. The Na–O bond lengths vary from 2.313(4) to 2.845(3) \AA , while the C–O bond lengths in HCOO^- are 1.214(4) and 1.237(5) \AA , respectively (Table S2†). These bond lengths are in good agreement with the reported borates and borate-formates.^{37,38} A 3D structure is finally formed showing a primitive cubic (pcu) net, in which each $(\text{B}_6\text{O}_{13})^{8-}$ unit connects with six other adjacent units (Fig. S4†). 9R pores are found in the $[001]$ direction. Na^+ and isolated HCOO^- units are filled in the spaces of the pores (Fig. 1b, c, d and S5†).

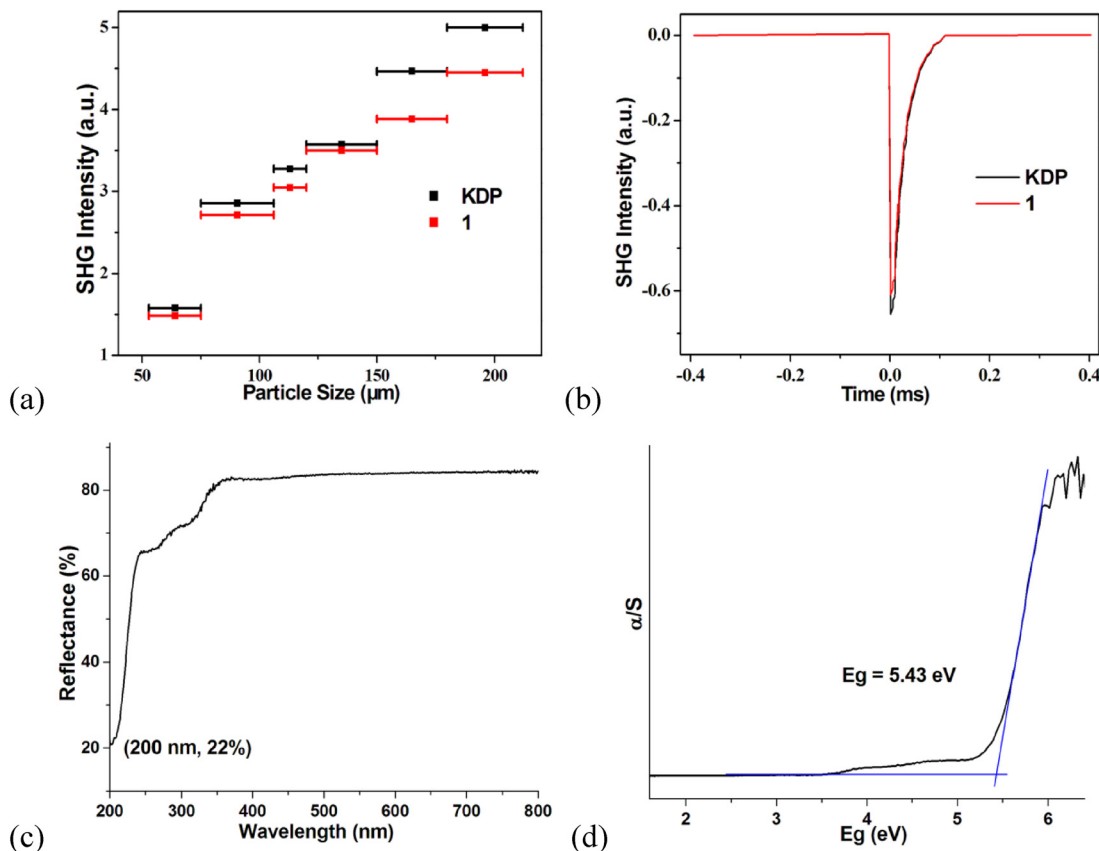


Fig. 2 (a) Phase-matching curves for **1** and KDP. (b) The SHG signals of **1** and KDP. (c) UV-vis diffuse-reflectance spectrum of **1**. (d) The band gap of compound **1**.

We performed powder SHG measurements on a Q-switched Nd:YAG laser at 1064 nm for its polar space group $P2_12_12_1$. The SHG signal intensity of **1** is moderate and comparable to the KDP (0.93KDP). Furthermore, compound **1** is phase-matchable as its SHG signal intensity gradually increased with larger particle size (Fig. 2a and b). The UV-vis diffuse-reflectance spectrum shows that compound **1** has a large transmission in the UV-vis region and a transparency of about 22% at 200 nm. The band gap is 5.43 eV as calculated by the Kubelka–Munk function, which corresponds to a UV cutoff edge at about 228 nm (Fig. 2c and d). These features suggest that compound **1** is a potential NLO crystal in the UV region.

To theoretically understand the optical properties of **1**, we performed first-principles density functional theory (DFT) calculations.³⁹ Fig. 3a shows the electronic band structure and the partial density of states (PDOS) for **1**. As shown in Fig. 3a, **1** is a direct-gap crystal with both the valence band maximum (VBM) and the conduction band minimum (CBM) at the Γ point. The theoretical band gap is 5.25 eV, which is slightly less than the experimental band gap of 5.43 eV (Fig. 2d). The difference in the band gap is due to the well-known underestimation of the energy band gap in the LDA calculation. To match the experimental band gap, the scissor correction of 0.18 eV was used in the optical calculations. Fig. 3b shows the dynamic SHG coefficients of **1**. Based on the D_2 symmetry, **1** has six non-zero SHG coefficients (*i.e.*, xyz , xzy , yzx , yxz , zxy ,

zyx ; the description of x , y , and z is given in Fig. 3c). With the limit of intrinsic permutation symmetry (*i.e.*, $xyz = xzy$, $yzx = yxz$, $zxy = zyx$), the independent SHG coefficients reduce to three elements (*i.e.*, xyz , yzx , zxy). As shown in Fig. 3b, in the optical region with the input photon wavelength (ω) larger than the visible wavelength (~ 400 nm), the SHG coefficients have no obvious dispersion, suggesting that **1** is suitable for a very long wavelength range. When the ω is larger than 400 nm (~ 3 eV), we observe some clear resonance enhancements. In these resonance enhancements, the linear absorption possibly takes place because the band gap is 5.43 eV, and thus these should be avoided in the nonlinear optical measurements. At 1064 nm, the largest SHG coefficient d_{25} is 0.46 pm V^{-1} , which is close to $d_{36}(\text{KDP}) \times 1.2$ and in agreement with the experimental measurement $d_{36}(\text{KDP}) \times 0.93$. The PDOS indicates that the B–O and HCOO^- units are responsible for the optical properties of **1**, because the electronic transitions between the VB and CB states close to the band gap generally determine the optical response;⁴⁰ these results are similar to our recent work.^{31b,32} The HCOO^- units occupying only the channels contribute significantly to the states near the CB edge (Fig. 3a), suggesting that the HCOO^- units contribute significantly to the nonlinear polarization, which is consistent with previous theoretical reports.²⁷ Furthermore, the frontier orbitals (Fig. 3c) at the Γ point show a clear charge transfer from the B–O units to the HCOO^- units. Finally, to inspect the phase-

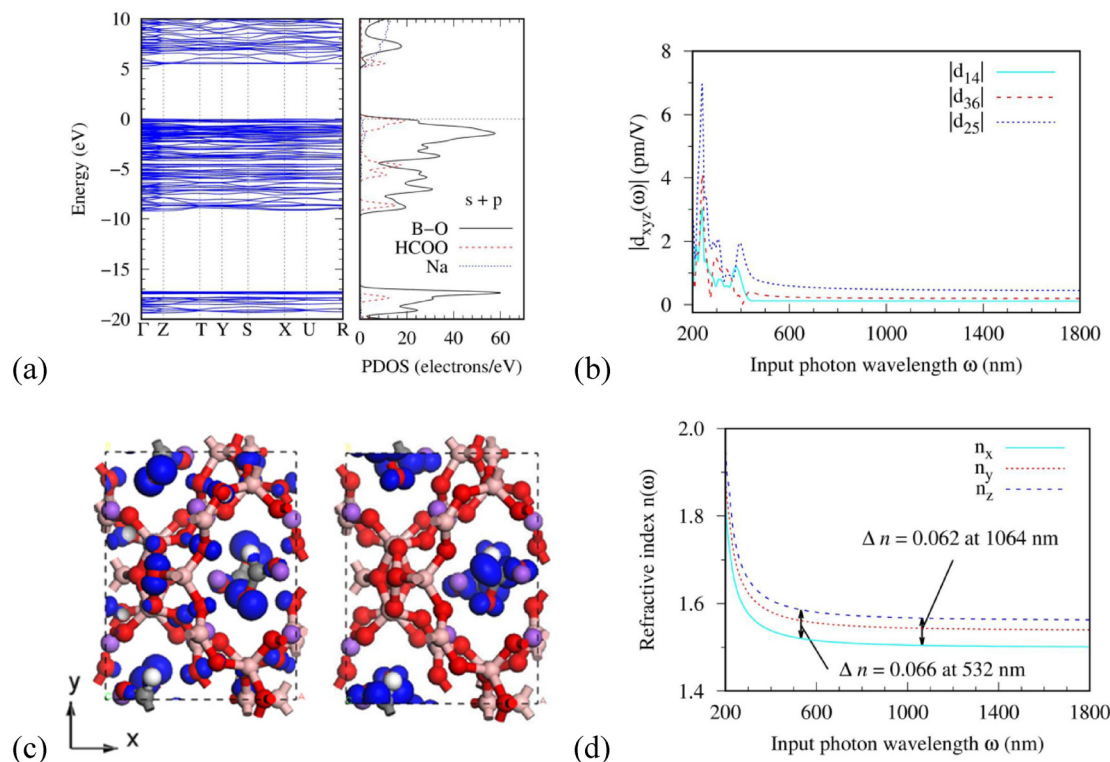


Fig. 3 (a) Electronic band structure and PDOS for **1**. (b) Dynamic second harmonic generation coefficients $|d_{xyz}|$. (c) The highest occupied orbital (left) and the lowest unoccupied orbital (right) at the Γ point. Color code: B, pink; O, red; Na, purple; C, dark grey; H, white; molecular orbital, blue. (d) Calculated refractive index n for **1**.

matching conditions, we show the calculated refractive index for **1** in Fig. 3d. We focus on the refractive indices at 1064 and 532 nm because **1** is a biaxial crystal.⁴¹ At 1064 nm, the three principal indices (n_x , n_y , and n_z) are 1.5044, 1.5435, and 1.5669, respectively, and at 532 nm, they are 1.5204, 1.5611, and 1.5861, respectively. By sorting the three principal indices into $n_z > n_y > n_x$, we obtain the third refractive-index condition pointed out by M. V. Hobden,⁴¹ that is, $n_x^{2\omega} < 1/2(n_x^\omega + n_y^\omega)$, $n_y^{2\omega} > 1/2(n_y^\omega + n_z^\omega)$, $n_z^{2\omega} > n_z^\omega > n_y^{2\omega} > n_y^\omega > n_x^{2\omega} > n_x^\omega$, where n^ω and $n^{2\omega}$ indicate the refractive indices at 1064 and 532 nm, respectively. Furthermore, as shown in Fig. 3d, Δn is between 0.06 and 0.07 at 1064 and 532 nm, which is a suitable birefringence required for meeting the phase-matching conditions in the UV region.^{2,42}

Conclusions

In summary, we have synthesized a new polar sodium borate-formate under surfactant-thermal conditions. The $(\text{B}_6\text{O}_{13})^{8-}$ cluster is observed and it connects with six other neighboring units to form a 3D anionic framework with 9R channels, with Na^+ and isolated HCOO^- units being found in the channels. This polar sodium borate-formate exhibits a UV absorption edge, moderate birefringence and SHG responses, and is phase-matchable. These characteristics indicate that **1** is a potential UV NLO material. DFT calculations show that the nonlinear optical response originates from the B–O units and HCOO^- ions. Our work indicates that the alkali metal borate-formate system may be suitable for finding UV NLO materials.

Conflicts of interest

There are no conflicts to declare.

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