

## RESEARCH ARTICLE

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# Y(C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O: strategic integration of ligand substitution and π-conjugated group linkage in sulfates for enhanced ultraviolet nonlinear optical properties

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Ultraviolet (UV) nonlinear optical (NLO) materials are critical for laser frequency conversion to extend wavelength ranges. Sulfates have emerged as a promising family of UV NLO materials, yet their NLO performance is constrained by the low optical anisotropy of the constituent [SO<sub>4</sub>]<sup>2-</sup> groups. In this study, we investigate the [C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>]<sup>-</sup> group, formed by substituting a ligand of the non-π-conjugated [SO<sub>4</sub>]<sup>2-</sup> unit with a π-conjugated benzene ring, and demonstrate that this group has a strong second harmonic generation (SHG) response and large birefringence. Leveraging this optimized structural unit, we successfully synthesize the first UV NLO benzenesulfonate, Y(C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. This compound exhibits enhanced UV optical properties, including a short cutoff edge of 280 nm, a relatively large SHG efficiency (0.8 × KDP), and a large birefringence of 0.16 at 1064 nm. This work not only presents Y(C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O as a competitive UV NLO material, but also highlights the [C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>]<sup>-</sup> group as a highly effective structural motif for the future development of advanced UV NLO materials.

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## Introduction

Nonlinear optical (NLO) crystals are indispensable materials for coherent laser frequency conversion, playing a pivotal role in the rapid development of laser technology and its diverse applications, including ultrafine spectroscopy, entangled photon pair generation, environmental monitoring, and explosive detection.<sup>1–3</sup> To date, commercial NLO materials such as LBO (LiB<sub>3</sub>O<sub>5</sub>),<sup>4</sup> β-BBO (β-BaB<sub>2</sub>O<sub>4</sub>),<sup>5</sup> KTP (KTiOPO<sub>4</sub>),<sup>6</sup> KDP (KH<sub>2</sub>PO<sub>4</sub>)<sup>7</sup> and LN (LiNbO<sub>3</sub>)<sup>8</sup> have demonstrated excellent performance, characterized by suitable transparency ranges, large second-harmonic generation (SHG) responses, and moderate birefringence. These properties stem from the well-arranged NLO-active units within their structures, as elucidated by, *e.g.*, anionic group theory.<sup>9</sup> However, as laser technology continues to evolve, the discovery of new NLO crystals with good performance has been imperative. Yet, surpassing the performance of commercial crystals using traditional structural units remains a great challenge. Thus, the development of new NLO active

units is crucial for the exploration of next-generation NLO materials.<sup>10–15</sup>

Very recently, the non-π-conjugated [SO<sub>4</sub>]<sup>2-</sup> unit has garnered significant attention owing to its ability to achieve wide bandgaps, strong SHG responses and rich structural diversity. For example, Zhao *et al.* reported NH<sub>4</sub>NaLi<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>,<sup>16</sup> which exhibits a bandgap of 5.5 eV and a SHG response of 1.1 × KDP. Similarly, Zou *et al.* demonstrated CsSbF<sub>2</sub>SO<sub>4</sub><sup>17</sup> with a bandgap of 4.76 eV and a SHG response of 3 × KDP. Despite their promising properties, materials whose anionic groups are exclusively composed of non-π-conjugated [SO<sub>4</sub>]<sup>2-</sup> groups typically exhibit low optical anisotropy. This is attributed to their nearly isotropic responses to external optical fields. This limitation typically results in small birefringence (~0.02), which would hinder the achievement of short phase matching wavelengths.

To address the challenge of low birefringence in sulfates, two primary strategies – typically employed separately – have been developed. The first strategy involves the incorporation of additional units with large structural anisotropy while maintaining the integrity of [SO<sub>4</sub>]<sup>2-</sup> groups. For instance, planar π-conjugated groups, *e.g.*, the [BO<sub>3</sub>]<sup>3-</sup> group, and stereochemically active lone pair (SCALP) cation-centred units, *e.g.*, the [SbO<sub>3</sub>Cl<sub>2</sub>] group, have been successfully introduced into sulfates, achieving large birefringence values. Notable examples include (NH<sub>4</sub>)<sub>2</sub>B<sub>4</sub>SO<sub>10</sub> (0.056 at 1064 nm)<sup>18</sup> reported by Pan

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*et al.* and  $\text{RbSbSO}_4\text{Cl}_2$  (0.112 at 1064 nm)<sup>19</sup> reported by Zou *et al.* The second strategy focuses on enhancing polarizability anisotropy by modifying the ligands of the  $[\text{SO}_4]^{2-}$  tetrahedron. Partial substitution of oxygen atoms in  $[\text{SO}_4]^{2-}$  with other atoms or groups can disrupt the symmetry of the tetrahedron and deform its electron cloud structure, thereby improving polarizability anisotropy. This approach has led to the development of units such as  $[\text{SO}_3\text{F}]^-$ ,  $[\text{SO}_3\text{CH}_3]^-$ ,  $[\text{SO}_3\text{CF}_3]^-$  and  $[\text{SO}_3\text{NH}_2]^-$ , which exhibit relatively large birefringence, enabling short phase-matching wavelengths in NLO sulfates. For example, Ye *et al.* reported  $\text{C}(\text{NH}_2)_3\text{SO}_3\text{F}$ <sup>20</sup> with a birefringence of 0.133; Lin *et al.* achieved a birefringence of 0.05 in  $\text{CsSO}_3\text{CF}_3$ <sup>21</sup> and Luo *et al.* discovered  $\text{Sr}(\text{SO}_3\text{NH}_2)_2$ <sup>22</sup> with a birefringence of 0.05.

In this work, we combine the two aforementioned strategies by substituting one oxygen atom in the  $[\text{SO}_4]^{2-}$  tetrahedron with an additional group exhibiting large structural anisotropy, aiming to develop a new NLO active unit. Specifically, given its substantial hyperpolarizability, the planar  $\pi$ -conjugated benzene ring is chosen as the additional group. The  $[\text{C}_6\text{H}_5\text{SO}_3]^-$  group, which fuses the  $\pi$ -conjugated benzene ring with the non- $\pi$ -conjugated  $[\text{SO}_4]^{2-}$  tetrahedron, is then constructed and subjected to theoretical investigation. This innovative group exhibits both large hyperpolarizability and significant polarizability anisotropy. Based on this optimized structural unit, we successfully synthesize the first UV NLO benzenesulfonate,  $\text{Y}(\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$ . This compound crystallizes in a non-centrosymmetric space group and exhibits a wide UV cutoff edge of 280 nm, a relatively large powder SHG response of  $0.8 \times \text{KDP}$ , a large birefringence of 0.16 at 1064 nm and a short phase matching wavelength of 300 nm, indicating its potential as a UV NLO material. Furthermore, first principles calculations are performed to elucidate its NLO mechanism, highlighting the  $[\text{C}_6\text{H}_5\text{SO}_3]^-$  group as a promising NLO active unit for further exploration and material design.

## Experimental section

### Reagents

Benzenesulfonic acid (98%, Aladdin) and  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  (97%, Aladdin) were used directly in the synthesis process without further processing.

### Synthesis

Benzenesulfonic acid (7.11 g, 4.5 mmol) was dissolved in 15 mL of deionized water.  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  (2.925 g, 1.5 mmol) was then added to the solution, and the mixture was stirred thoroughly until complete dissolution was achieved. The solution was permitted to evaporate gradually at a controlled temperature of 25 °C, which effectively facilitated the crystallization process. After a period of ten days, the formation of single crystals of  $\text{Y}(\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$  was distinctly observed, as they precipitated and settled at the bottom of the beaker.

### Single-crystal structure analysis

Single crystals of suitable dimensions ( $0.01 \times 0.01 \times 0.01 \text{ mm}^3$ ) were carefully selected for X-ray diffraction (XRD) analysis. Data collection was performed using a Bruker D8 Quest diffractometer equipped with a Mo  $\text{K}\alpha$  radiation source ( $\lambda = 0.71073 \text{ \AA}$ ). Indexing and data integration were carried out using the APEX3 software suite, employing the difference vectors method. Absorption corrections were applied using the multi-scan method implemented in the SADABS program. The space group was determined using XPREP, which is integrated into the APEX3 package.<sup>23</sup>

The crystal structures were initially solved using SHELXT and subsequently refined with SHELXL-2014, employing full-matrix least-squares refinement on  $F^2$ . Anisotropic displacement parameters were included in this refinement process. The structural frameworks of  $\text{Y}(\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$  were visualized and analyzed using the OLEX2 software package. The positions of individual atoms were refined by least-squares minimization using the SHELXL-2014 refinement package.<sup>24</sup> Finally, the PLATON program was used to verify the structural symmetry and authenticity.

### Powder X-ray diffraction

The powder XRD (PXRD) measurements of  $\text{Y}(\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$  were carried out on a Bruker D8 focus diffractometer ( $\lambda = 1.5418 \text{ \AA}$  and  $2\theta = 5\text{--}80^\circ$ ). The scanning step was set to  $0.05^\circ$ , and the fixed counting time was set to 0.5 s per step.

### UV-vis-NIR diffuse reflectance spectra

The UV-vis diffuse reflection data were recorded at room temperature using powder samples and an Agilent Cary 7000 UV/vis/NIR spectrophotometer over 200–2000 nm.  $\text{BaSO}_4$  was chosen as the back base.

### Birefringence

Birefringence was measured using a Nikon Eclipse polarizing microscope E200MV POL under a visible light filter. The birefringence was calculated using the formula  $\Delta n = \Delta R/T$ , where  $\Delta R$ ,  $\Delta n$ , and  $T$  represent the optical path difference, the birefringence, and the thickness of the crystal, respectively. A transparent strip crystal was chosen to ensure accuracy. The thickness of the sample was measured using a Bruker Smart Apex II.

### Thermal analysis

Thermogravimetric analysis (TGA) was performed on a HITACHI STA 200 instrument. The crystal sample was heated in the temperature range of 30–800 °C at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ .

### Powder SHG measurement

The powder SHG of  $\text{Y}(\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$  was measured using the Kurtz–Perry approach<sup>25</sup> on a Q-switched Nd:YAG laser (1064 nm). Polycrystalline samples of  $\text{Y}(\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$  were ground into different particle size ranges (10–60, 60–100,



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100–150, and 200–250  $\mu\text{m}$ ). Accordingly,  $\text{KH}_2\text{PO}_4$  (KDP) samples with the same particle size ranges were tested for reference.

## Computational method

The electronic and optical properties of the  $[\text{C}_6\text{H}_5\text{SO}_3]^-$  group and related  $[\text{SO}_4]^{2-}$  based groups, including the LUMO–HOMO (lowest unoccupied molecular orbital–highest occupied molecular orbital) gaps, hyperpolarizability ( $\beta$ ) and polarization anisotropy ( $\delta$ ) were investigated using Gaussian 16 software.<sup>26,27</sup> The calculations were performed using the B3LYP functional with the 6-31G basis set, a computational setting widely validated and employed in quantum chemical calculations.<sup>28</sup>

The CASTEP program based on density functional theory (DFT)<sup>29</sup> was employed to calculate the linear and nonlinear optical properties in  $\text{Y}(\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$ . The exchange–correlation (XC) functional is described by the generalized gradient approximation (GGA) with Perdew, Burke and Ernzerhof (PBE) functionals.<sup>30</sup> The ion/electron interactions are modelled using norm-conserving pseudopotentials for all the constituent elements. In this model, C  $2s_22p_2$ , H  $1s_1$ , O  $2s_22p_4$ , S  $3s_23p_4$  and Y  $4d_15s_2$  electrons are treated as the valence electrons. A kinetic energy cutoff of 750 eV and Monkhorst–Pack  $k$ -point meshes spanning less than  $0.07 \text{ \AA}^{-3}$  in the Brillouin zone were chosen to ensure sufficient accuracy for the present purposes.

The SHG coefficients were calculated using the method developed by our group. In addition, the band-resolved SHG coefficient and SHG-weighted density analyses were performed to intuitively visualize the electronic orbitals and structural motifs contributing to SHG in real space.<sup>31</sup> Our previous study revealed that the occupied-state contribution *via* virtual electronic transitions dominates the SHG effect in materials.<sup>32</sup>

## Results and discussion

The  $[\text{C}_6\text{H}_5\text{SO}_3]^-$  group can be viewed as a benzene ring replacing one O atom in the  $[\text{SO}_4]^{2-}$  group. We theoretically investigated its LUMO–HOMO gap ( $E_{\text{LUMO-HOMO}}$ ), hyperpolarizability ( $\beta$ ) and polarization anisotropy ( $\delta$ ), and compared it with those in related  $[\text{SO}_4]^{2-}$  based groups, including  $[\text{SO}_4]^{2-}$ ,  $[\text{SO}_3\text{NH}_2]^-$ ,  $[\text{SO}_3\text{F}]^-$ , and  $[\text{SO}_3\text{CH}_3]^-$ . Their structures and calculated results are shown in Fig. 1. As shown, the  $[\text{SO}_4]^{2-}$ ,  $[\text{SO}_3\text{NH}_2]^-$ ,  $[\text{SO}_3\text{F}]^-$ , and  $[\text{SO}_3\text{CH}_3]^-$  groups exhibit a tetrahedral configuration, considering the small size of the H atom, while the  $[\text{SO}_3\text{CF}_3]^-$  group adopts a distorted tetrahedral geometry. In comparison, the  $[\text{C}_6\text{H}_5\text{SO}_3]^-$  group features a planar ring connected to a  $[\text{SO}_3]$  triangular pyramid. These structural differences lead to significant variations in their optical properties. Notably, the NLO-related properties of the  $[\text{C}_6\text{H}_5\text{SO}_3]^-$  group are studied for the first time, although its polarizability anisotropy has been previously highlighted.<sup>33</sup>

The results demonstrate that the  $[\text{C}_6\text{H}_5\text{SO}_3]^-$  group exhibits superior  $\beta$  and  $\delta$ , which are approximately two and ten times larger, respectively, than those of the related tetrahedral

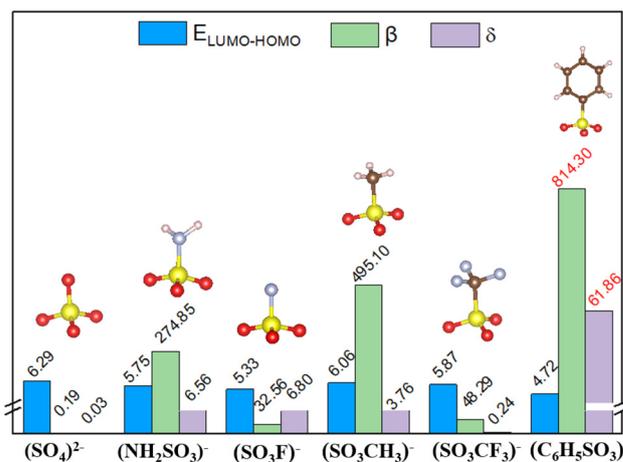


Fig. 1 Geometry and key NLO properties ( $E_{\text{LUMO-HOMO}}$  (eV),  $\beta$  (a.u.) and  $\delta$  (a.u.)) of  $[\text{SO}_4]^{2-}$ ,  $[\text{SO}_3\text{NH}_2]^-$ ,  $[\text{SO}_3\text{F}]^-$ ,  $[\text{SO}_3\text{CH}_3]^-$ ,  $[\text{SO}_3\text{CF}_3]^-$  and  $[\text{C}_6\text{H}_5\text{SO}_3]^-$ .

groups. Meanwhile, a wide  $E_{\text{LUMO-HOMO}}$  can be maintained even after the introduction of the  $\pi$ -conjugated benzene ring, which is conducive to applications in the UV range. These findings indicate that the incorporation of the  $[\text{C}_6\text{H}_5]$  moiety significantly enhances the  $\beta$  and  $\delta$  of the  $[\text{SO}_4]^{2-}$  group, highlighting the  $[\text{C}_6\text{H}_5\text{SO}_3]^-$  group as a promising UV NLO active group.

Based on the benzenesulfonic  $[\text{C}_6\text{H}_5\text{SO}_3]^-$  unit, the first UV NLO benzenesulfonate,  $\text{Y}(\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$ , was successfully synthesized. Single crystals of  $\text{Y}(\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$  were grown using a simple solution evaporation method and a single crystal with the dimensions of  $10 \times 10 \times 2 \text{ mm}^3$  was obtained, as shown in Fig. 2a, which demonstrated a good crystal growth habit. Single-crystal XRD measurements were performed to solve and refine the crystal structure of  $\text{Y}(\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$ .

Detailed structural information including crystallographic data and refinement parameters, crystal data and structure

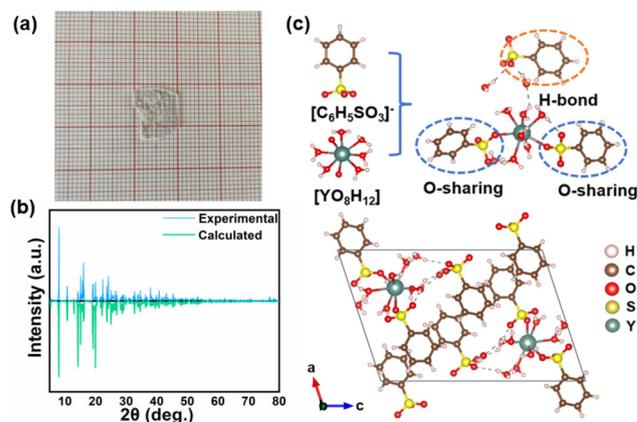


Fig. 2 (a) Single crystal photograph of a crystal of  $\text{Y}(\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$ . (b) Experimental and calculated XRD patterns of  $\text{Y}(\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$ . (c) Crystal structure of  $\text{Y}(\text{C}_6\text{H}_5\text{SO}_3)_3 \cdot 9\text{H}_2\text{O}$ .

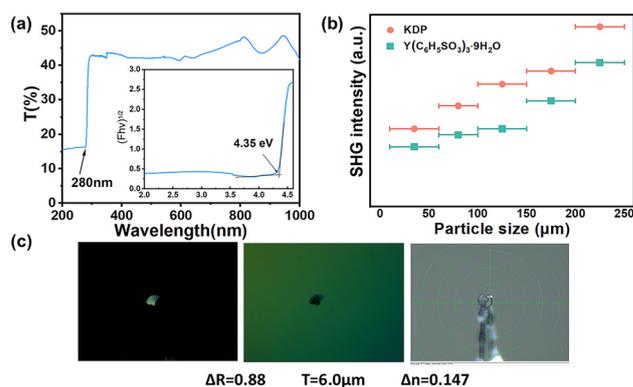


refinement, atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, selected bond lengths, selected bond angles, and hydrogen atom coordinates with isotropic displacement parameters is provided in Table 1 and Tables S1–S6.

The PXRD pattern of the title compound is shown in Fig. 2b, which is in good agreement with the calculated results of the single crystal XRD data, indicating the high purity of the obtained samples. The crystal structure of  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$  is displayed in Fig. 2c. This compound crystallizes in the non-centrosymmetric monoclinic space group of  $P2_1$  (no. 4). The asymmetric unit comprises 18, 33, 18, 3 and 1 crystallographically independent C, H, O, S and Y atoms, respectively. Six C and five H atoms constitute a benzene ring, which is further connected with  $[SO_3]$  and forms a benzenesulfonic  $[C_6H_5SO_3]^-$  unit. The Y atom is coordinated by eight O atoms, two of which originate from the  $[C_6H_5SO_3]^-$  units, while the remaining six are provided by the  $H_2O$  molecule. As shown in Fig. 2c, the  $[C_6H_5SO_3]^-$  groups are connected to the Y atom in two ways: one is by sharing the oxygen atom on the  $[C_6H_5SO_3]^-$  group, and the other is by hydrogen bonding mediated by water molecules nearby. The  $[C_6H_5SO_3]^-$  groups are alternately arranged on the  $a$ - $c$  plane, forming a porous structure. The  $[YO_8H_{12}]$  groups occupy the space between coordination chains and hydrogen bonding in stabilizing the crystal structure.

### Optical properties

The UV-vis diffuse spectrum of the title compound is displayed in Fig. 3a. Clearly,  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$  exhibits good transmittance extending into the UV region. Its UV cutoff edge is located at 280 nm, corresponding to a wide band gap of 4.35 eV,<sup>34</sup> indicating its potential for applications in the UV range. The UV cutoff edge of this compound is comparable to those



**Fig. 3** (a) Transmittance of  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$ . (b) SHG response of  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$ . (c) Photos of a birefringence test of  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$ .

of other UV NLO materials, such as  $Li_2(H_2C_4N_2O_3) \cdot 2H_2O$  (260 nm),<sup>35</sup>  $[C(NH_2)_3]_2SO_3S$  (254 nm),<sup>36</sup> and  $[C(NH_2)_3]_3PO_4 \cdot 2H_2O$  (250 nm),<sup>37</sup> while it is smaller than those of  $(NH_4)_2PO_3F$  (177 nm),<sup>38</sup>  $Cs_3[(BOP)_2(B_3O_7)_3]$  (165 nm),<sup>39</sup> and  $Rb_3B_{11}P_2O_{23}$  (168 nm).<sup>40</sup>

The SHG response of  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$  was evaluated using the Kurtz–Perry method under 1064 nm laser irradiation, with KDP as the reference. As shown in Fig. 3b, the SHG signal of  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$  increases with particle size in the range from 10 to 250  $\mu m$ , confirming its phase-matching capability. Finally, the SHG response reaches approximately  $0.8 \times$  KDP, a value comparable to those of  $Ba_5P_6O_{20}$  ( $0.8 \times$  KDP),<sup>41</sup>  $\beta-(C_2H_5N_4)(NO_3)$  ( $0.8 \times$  KDP),<sup>42</sup> and  $K_7CaY_2(B_5O_{10})_3$  ( $1 \times$  KDP),<sup>43</sup> and smaller than those of  $Rb_3Hg_2(SO_4)_3Cl$  ( $1.5 \times$  KDP)<sup>44</sup> and  $NH_4B_4O_6F$  ( $3 \times$  KDP).<sup>45</sup> It should be emphasized that, despite the large  $\beta$  of the  $[C_6H_5SO_3]^-$  unit, the NLO-unfavorable arrangement of these units in  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$  may limit further enhancement of the SHG response.

The birefringence of  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$  was measured with a polarizing microscope (Fig. 3c). The optical path difference  $R$  was found to be 880 nm and the crystal thickness  $T$  was about 6.0  $\mu m$ . Using the equation  $\Delta n = \Delta R/T$ , the birefringence was determined to be 0.147. This value exceeds those of commercial UV NLO materials, such as  $BBO$ <sup>46</sup> and  $LBO$ ,<sup>4</sup> and is comparable to those of recently reported UV NLO materials, e.g.,  $Zn(SCN)_2$  (0.164 at 546 nm),<sup>47</sup>  $Na[BF_2(CN)_2]$  (0.152 at 546.1 nm),<sup>48</sup> and  $Rb_2SbFP_2O_7$  (0.15 at 546 nm).<sup>49</sup> From a structural perspective, the large birefringence can be attributed to the planar arrangement of the  $\pi$ -conjugated benzene rings in  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$ .

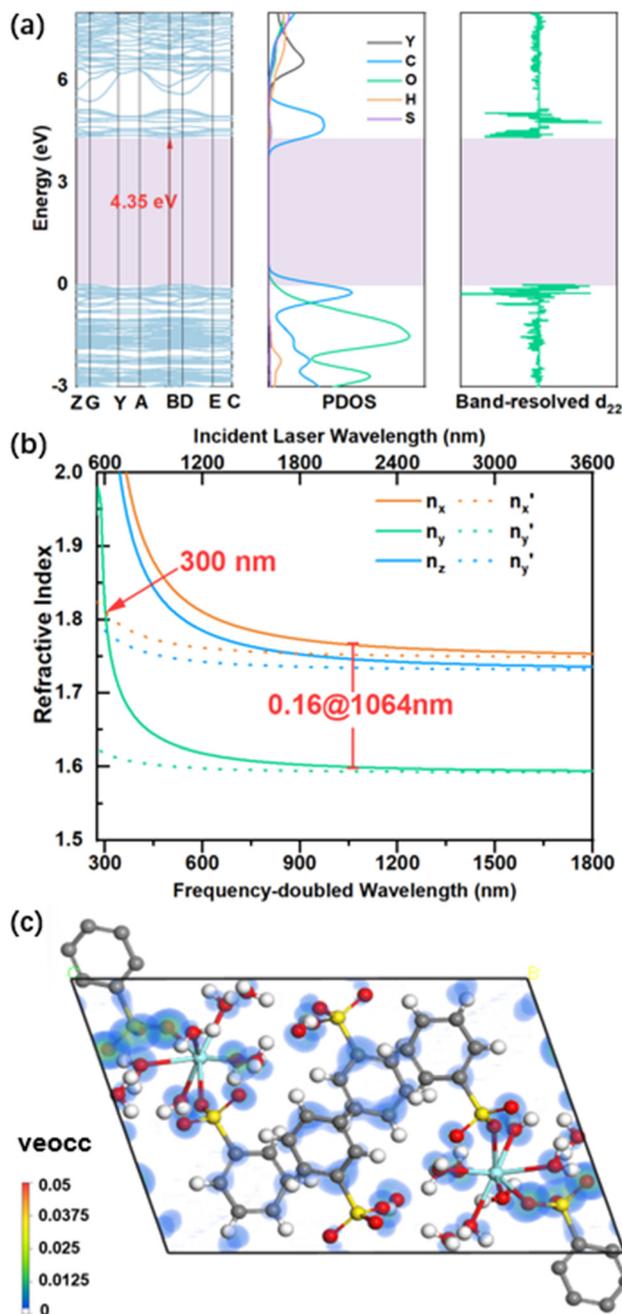
First-principles calculations were performed to evaluate the phase-matching behavior of  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$  (Fig. 4b). The calculated birefringence value at 1064 nm was 0.16, in good agreement with the experimental value. Based on the calculated refractive index dispersion curves, the shortest phase-matching wavelength was predicted to be 300 nm, indicating

**Table 1** Crystallographic data and refinement parameters for  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$

	$Y(C_6H_5SO_3)_3 \cdot 9H_2O$
Formula	C18 H33 O18 S3 Y
fw	722.53
Crystal system	Monoclinic
Space group	$P2_1$
$a/\text{\AA}$	11.8061(5)
$b/\text{\AA}$	7.4977(2)
$c/\text{\AA}$	17.4276(7)
$\alpha$ ( $^\circ$ )	90
$\beta$ ( $^\circ$ )	108.183
$\gamma$ ( $^\circ$ )	90
$V/\text{\AA}^3$	1472.34(10)
$Z$	2
$D_c$ ( $g\text{ cm}^{-3}$ )	1.630
$\mu$ (Mo-K $\alpha$ ) ( $mm^{-1}$ )	2.27
GOF on $F^2$	1.032
Flack factor	0.043(7)
$R_1, R_2$ ( $I > 2\sigma(I)$ ) <sup>a</sup>	0.0406, 0.0748

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





**Fig. 4** (a) Calculated band structure, partial density of states, and band-resolved  $d_{22}$ . (b) Calculated refractive index and birefringence. (c) The VE-occupied SHG density.

its potential for NLO applications in the UV region. According to the Kleinman symmetry restriction,  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$  possesses four independent SHG coefficients, *i.e.*,  $d_{14}$ ,  $d_{16}$ ,  $d_{22}$  and  $d_{23}$ . The first-principles values were  $0.07 \text{ pm V}^{-1}$ ,  $0.29 \text{ pm V}^{-1}$ ,  $-0.50 \text{ pm V}^{-1}$  and  $0.04 \text{ pm V}^{-1}$  for these SHG coefficients, respectively, with the maximum value of  $d_{22} = -0.50 \text{ pm V}^{-1}$ , which agree well with the experimental result. To further elucidate the relationship between structure and NLO performance,

the electronic band structure and partial density of states (PDOS) in  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$  were calculated, and the band-resolved analysis of the  $d_{22}$  coefficient was performed. As shown in Fig. 4a,  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$  is a direct bandgap compound. The orbitals located at both the conduction band minimum and the valence band maximum are occupied by O and C from the  $[C_6H_5SO_3]^-$  group. Meanwhile, the band-resolved plot shows that the orbitals nearby the band gap play dominant roles in determining the SHG response,  $d_{22}$  in this case, indicating that the  $[C_6H_5SO_3]^-$  group makes a dominant contribution to the NLO properties. To further clearly show the contributions of these orbitals, the SHG weighted densities are shown in Fig. 4c. Clearly, the orbitals are mainly from the  $[C_6H_5SO_3]^-$  group. For further exploration,  $[C_6H_5SO_3]^-$  groups may be used as good UV NLO active units and both larger SHG responses and birefringence are expected if they are arranged in an orderly manner.

## Conclusions

In conclusion, the integration of a  $\pi$ -conjugated benzene ring into a non- $\pi$ -conjugated  $[SO_4]^{2-}$  tetrahedron led to the discovery of the  $[C_6H_5SO_3]^-$  group as an exceptional UV NLO active unit, characterized by its large hyperpolarizability and significant polarizability anisotropy. Capitalizing on this discovery, we successfully synthesized the first UV NLO benzenesulfonate,  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$ . This compound exhibits a wide bandgap, a relatively strong SHG response, a significant birefringence, and a short phase-matching wavelength, collectively highlighting its potential as a promising UV NLO material. Additionally, first-principles calculations were conducted to unravel the underlying NLO mechanism. This work not only introduces a new candidate for UV NLO materials but also establishes the  $[C_6H_5SO_3]^-$  group as a high-performance UV NLO active unit for further exploration and material design.

## Conflicts of interest

There are no conflicts of interest to report.

## Data availability

The data supporting this article have been included as part of the SI.

TG/DTG curves of  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$ , crystal data and structure refinement, atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ), anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ), selected bond lengths, selected bond angles (deg), hydrogen atom coordinates ( $\text{\AA} \times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) of  $Y(C_6H_5SO_3)_3 \cdot 9H_2O$ . CCDC 2366861 contains the supplementary crystallographic data for this paper. See DOI: <https://doi.org/10.1039/d5qi01311a>.

CCDC 2366861 contains the supplementary crystallographic data for this paper.<sup>50</sup>



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