

## Supporting information

### Crystal Growth and Characterization of A New Polymorph of Bismuth Trithiourea Chloride

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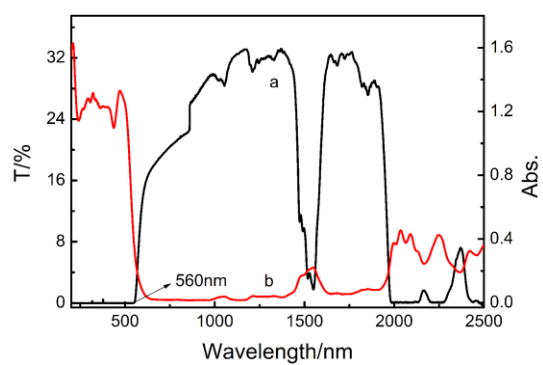
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The space groups of  $\alpha$ -BTC and  $\beta$ -BTC in the article are chosen as noncentrosymmetric in the structure analysis because of the following facts: for the  $\alpha$ -BTC, powder second harmonic generation (SHG) tests indicated its effective SHG coefficient to be 1/6 that of KDP. Meanwhile, reference 18 mentioned that  $\beta$ -BTC was noncentrosymmetric and exhibited NLO properties. When the anisotropic thermal factors of lighter elements (C-N) of both  $\alpha$ -BTC and  $\beta$ -BTC were refined, they went either too large or negative. Therefore we refined them isotropically and the H atoms were added to N by HFIX. The crystallographic data of  $\beta$ -BTC is shown in Table S1.

**Table S1.** Crystallographic data of  $\beta$ -BTC

	$\beta$ -BTC
Formula	C <sub>3</sub> H <sub>12</sub> N <sub>6</sub> S <sub>3</sub> BiCl <sub>3</sub>
M	543.70
Temperature	299(2)K
Crystal System	Trigonal
Space group	<i>P</i> 3(#143)
<i>a</i> /Å	13.5930(11)
<i>b</i> /Å	13.5930(11)
<i>c</i> /Å	7.1406(11)
$\beta$ /deg	90.00
Cell volume/Å <sup>3</sup>	1142.6(2)
Z	3
Nref	3491
R1 (all data)	0.0672
wR2 (all data)	0.0765



**Figure S1** The optical transmission(a) and diffuse reflection(b) spectra of  $\beta$ -BTC