

Supporting information

Ba₃(C₃N₃O₃)₂: A New Phase of Barium Cyanurate Containing Parallel π -Conjugated Groups as Birefringent Material Replacement for Calcite

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1. Experimental methods

Solid state reaction. The mixture of RbCNO and BaCl₂ with a molar ratio of 2.5 :1 was thoroughly ground and placed in a fused-silica tube. Also the ampoule was flame-sealed under a high vacuum of 10⁻³ Pa. The tube was heated to 423 K and left for 24 h with several intergrindings, and the samples were finally calcined at 590 K. The pure phase of **I** was successfully obtained after the remaining reagents of RbCNO and RbCl were washed away with dry ethanol.

Single crystal growth. The analytical pure starting reagent BaCl₂ and RbOCN were directly purchased from Alfa Aesar. All the manipulations were performed in an Ar-filled glove box with H₂O and O₂ contents less than 0.1 ppm. Appropriate amounts of BaCl₂ and RbOCN with a molar ratio of 1:3 were carefully ground and loaded into a fused-silica tube. The tube was flame-sealed under a high vacuum of 10⁻³ Pa and then placed in a temperature-controlled furnace. The tube was heated to 723 K within 10 h and left for 72 h to melt completely, and then slowly cooled to 373 K at a rate of 3 K/h, finally was cooled to room temperature by switching off the furnace.

Structure determination. Single-crystal X-ray diffraction data for Ba₃(C₃N₃O₃)₂ were collected at room temperature on a Rigaku XtaLAB Synergy four-circle diffractometer equipped with a HyPix-6000HE area detector using Mo K α (PhotonJet-S Mo 50w Microfocus) radiation source, with a frame time of 4 s, a frame width of 0.5°, and a detector distance of 32 mm. Data extraction and integration were carried out with use

of the CrysAlisPro software. Structure solution and refinement were carried out with use of the SHELXTL (version 6.12) program package.¹ Initial atomic positions were located by direct methods and refinements proceeded in a straightforward fashion. All atomic sites were confirmed to be fully occupied and exhibited reasonable displacement parameters. No additional symmetry was revealed by the ADDSYM routine in the PLATON suite programs.²

Powder X-ray diffraction. The powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Focus diffractometer equipped with Cu K α radiation at room temperature in the 2θ range of $10 - 70^\circ$.

UV-vis-IR diffuse reflectance spectrum. The spectrum of **I** was measured from 200 nm (6.2 eV) to 1500 nm (0.83 eV) on a Cary 7000 UV-vis-NIR spectrophotometer equipped with a diffuse reflectance accessory. A compacted pellet of BaSO₄ was used as a 100% reflectance standard. The absorption spectra were converted from reflectance spectra according to the Kubelka-Munk function: $\alpha/S = (1 - R)^2/2R$, where α , S and R are the absorption, scattering and reflectance coefficients, respectively.³

Infrared spectrum. Infrared (IR) spectroscopy was collected on a Varian Excalibur 3100 spectrometer in the $400 - 1800\text{ cm}^{-1}$ range. KBr and **I** samples with mass ratio about 100:1 were mixed thoroughly.

2. Computational methods

The density functional theory calculations of $\text{Ba}_2(\text{C}_3\text{N}_3\text{O}_3)_2$ were performed in the framework of CASTEP package⁴ by the plane-wave pseudo-potential methods. The total energy calculations including full structural optimizations were carried with the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional.⁵ The optimized norm-conserving pseudopotentials⁶ (Ba $4d^{10}6s^2$, C $2s^22p^2$, N $2s^22p^3$, O $2s^22p^4$) were used to simulate ion-electron interactions. A kinetic energy cutoff of 880 eV was chosen with Monkhorst-Pack k -point meshes ($4 \times 4 \times 2$) spanning less than $0.04/\text{\AA}^3$ in the first Brillouin zone.⁷ The convergence threshold for SCF tolerance is set as 1.0×10^{-9} eV/atom. The choice of these computational parameters is good enough to ensure the accuracy of the present purpose.^{8,9} Based on the optimized geometry structure, the dielectric function, refractive indices n and the birefringence Δn , were calculated using the Kramers–Kronig transformation. Some commercial birefringent materials (CaCO_3 , $\text{Ca}_3(\text{BO}_3)_2$ and $\beta\text{-BaB}_2\text{O}_4$) were also calculated as references. Moreover, the linear response method was employed to obtain the phonon dispersion of crystal to evaluate its stability.¹⁰ For phonon calculations, the ultrafine dispersion separation of $0.02/\text{\AA}^3$ and high cutoff energy of 1000 eV were adopted to make sure the good convergence.

Table S1. Crystal data and structure refinement for Ba₃(C₃N₃O₃)₂.

Empirical formula	Ba ₃ (C ₃ N ₃ O ₃) ₂
Formula weight	664.14
Crystal system	trigonal
Space group	$R\bar{3}$
a/Å	7.0934(2)
c/Å	20.1130(9)
Volume/Å ³	876.43(5)
Z	3
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	3.775
μ/mm^{-1}	10.040
F(000)	882.0
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	6.94 to 52.64
Index ranges	-8 \leq h \leq 8, -8 \leq k \leq 8, -24 \leq l \leq 24
Reflections collected	6301
Independent reflections	393 [R_{int} = 0.0322, R_{sigma} = 0.0102]
Data/restraints/parameters	393/0/33
Goodness-of-fit on F ²	1.129
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0333, wR_2 = 0.0914
Final R indexes [all data]	R_1 = 0.0335, wR_2 = 0.0915
Largest diff. peak/hole / e Å ⁻³	3.56/-1.00

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for $\text{Ba}_3(\text{C}_3\text{N}_3\text{O}_3)_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	Ueq
Ba1	0	0	0	0.0242(4)
Ba2	0	0	0.20168(4)	0.0174(3)
C1	0.1581(16)	0.4722(14)	0.0892(4)	0.033(2)
O1	0.0060(13)	0.2680(12)	0.0929(4)	0.0456(19)
N1	0.3575(16)	0.4869(13)	0.0894(4)	0.038(2)

Table S3. Selected bond lengths (Å) and angles (degree) for Ba₃(C₃N₃O₃)₂.

Ba1–O1(× 6)	2.651(8)	C1–N1(× 1)	1.322(14)
Ba2–C1(× 3)	3.228(11)	C1–N1(× 1)	1.365(14)
Ba2–O1(× 3)	2.884(8)	O–C–N	126.5(10)
Ba2–O1(× 3)	2.781(8)	O–C–N	109.6(9)
Ba2–N1(× 3)	3.018(9)	N–C–N	123.9(8)
C1–O1(× 1)	1.306(11)	C–N–C	116.1(8)

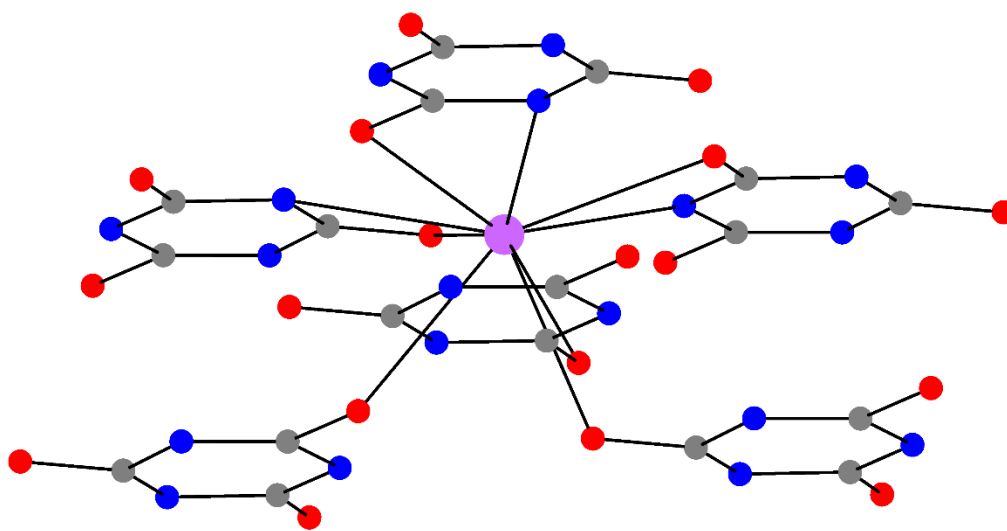


Figure S1. The coordination environment of Ba2 atom.

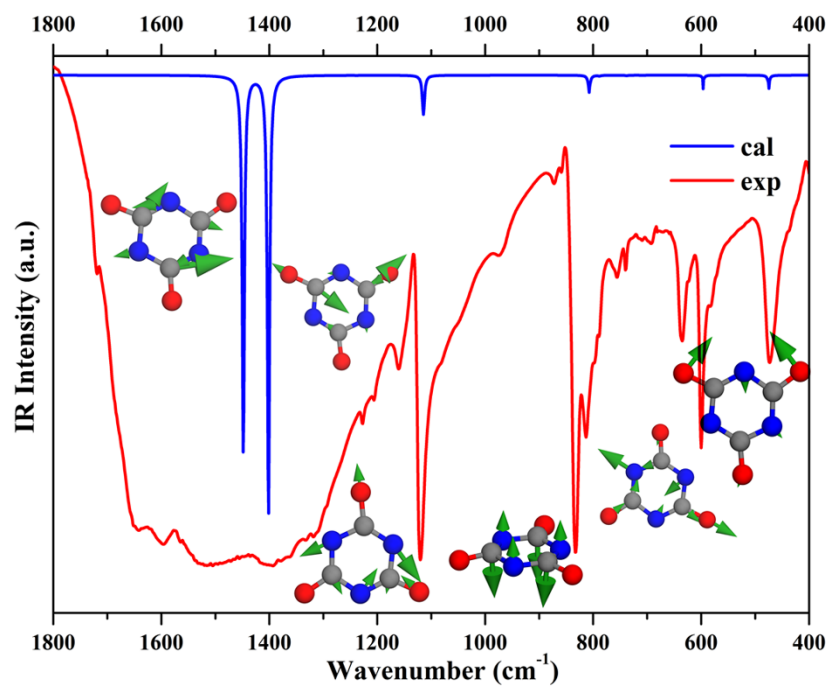


Figure S2. The IR spectroscopy of **I**.

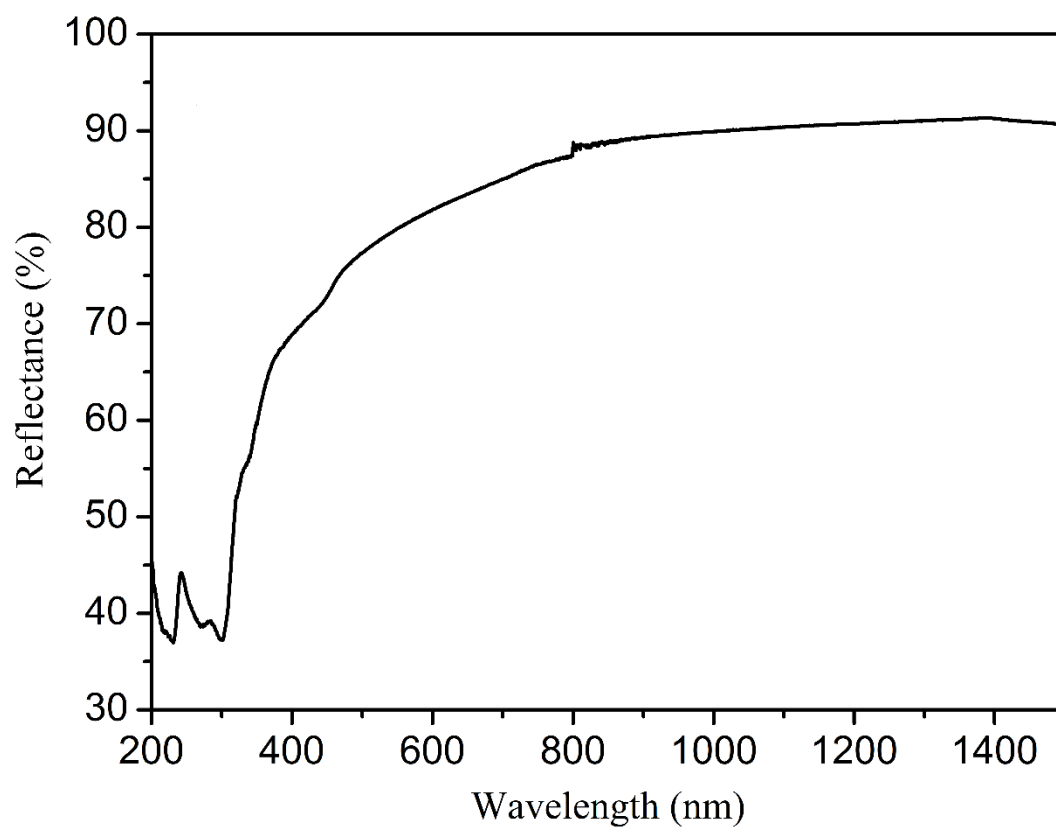


Figure S3. The reflectance of **I** in the range from 200 nm to 1500 nm.

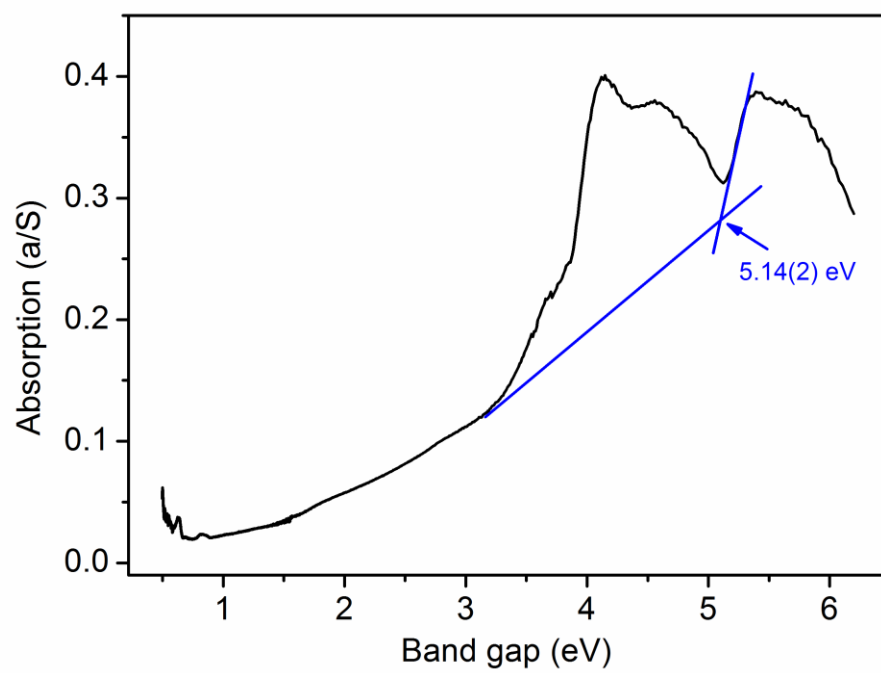


Figure S4. The band gap of **I**.

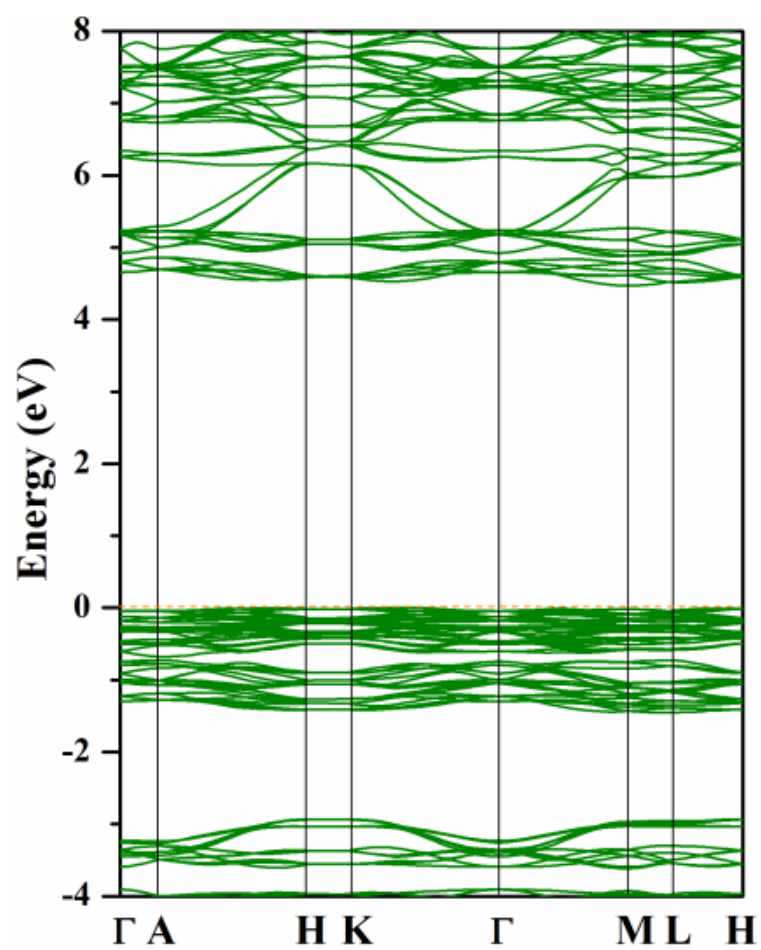


Figure S5. The electronic band structure of **I** calculated by the PBE functional

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