

Electronic Supplementary Information

(C₃N₆H₇)₂SiF₆·H₂O: an ultraviolet birefringent crystal exceeding the intrinsic energy gap of an organic reagent

Yaoguo Shen,^{*a} Yingwu Zhou,^a Xiaoling Xue,^a Hualiang Yu,^a Sangen Zhao^b and Junhua Luo^b

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^a College of Physics and Electronic Information Engineering, Minjiang University, Fuzhou, Fujian 350108, China. Email: shenyg@mju.edu.cn

^b State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

Reagents

$C_3N_6H_3$ (99%) and SbF_3 (98%) were purchased from Aladdin and used as received. The high borosilicate glass beaker is a necessary condition for the synthesis of target compound, because it can provide Si-based raw materials.

Synthesis of $(C_3N_6H_7)_2SiF_6 \cdot H_2O$ (**1**)

Crystals of **1** were synthesized by a simple evaporation technique of aqueous solution. The raw reactants of $C_3N_6H_3$ (0.126 g, 1 mmol) and SbF_3 (0.179 g, 1 mmol) were mixed together with deionized water (50 mL) in a high borosilicate glass beaker. The solution was stirred with a magnetic mixer for 30 minutes, and then filtered through a filter paper to obtain a clear, transparent liquid. The beaker was sealed with perforated plastic wrap and left to stand at room temperature for about 10 days. Curiously, colorless block crystals were attached to the wall of the glass beaker. Did the reactant react with the beaker? The structural determination confirmed our suspicions. The purity of the obtained product is confirmed by the powder X-ray diffraction (XRD) patterns, which were taken on a Rigaku MiniFlex II diffractometer (Cu $K\alpha$ radiation) in the range of $2\theta = 5^\circ\text{--}60^\circ$ with a step width of 0.01° and a sampling rate of 1°min^{-1} . The results agree well with the calculated XRD patterns from single-crystal XRD analysis (Figure 2a).

Single-Crystal Structure Determination

A colorless **1** crystal ($0.12 \times 0.11 \times 0.10 \text{ mm}^3$) was selected using an optical microscope for single-crystal XRD analysis. The diffraction data were collected by using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 297.14 (10) K on a ROD Synergy Custom DW system with a Hybrid Pixel Array Detector. The collection of the intensity data, cell refinement, and data reduction were carried out with the program CrysAlisPro.¹ Using Olex2,²⁻³ the structure was solved with SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL⁴ refinement package using Least Squares minimisation. Initially, we set the heavy Q peak to 'Sb' element, two anomalies occur: (1) most atoms are not positive definite. (2) The Sb–F bond lengths fall in the range of 1.66–1.67 Å, which much shorter than the reported value of about 1.92 Å. Therefore, other impurity should be introduced in the reaction solution. It can be speculated that the heavy Q peak may be Si based on the fact that the beaker is made up of high borosilicate glass. When the heavy Q peak is set to 'Si' element, the structure is reasonable after several rounds of refinement. Details of crystal parameters, data collection, and structure refinement are summarized in Table S1. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table S2, and the anisotropic displacement parameters are listed in Table S3. The selected bond distances and angles are presented in Table S4–S5. Hydrogen bonds are listed in Table S6.

Thermal Stability Analysis

The thermogravimetric (TG) and differential thermal analysis (DTA) of **1** was carried out on a NETZSCH STA 449F3 simultaneous analyzer. About 6.372 mg of **1** was placed in Al_2O_3 crucibles, heated at a rate of $15 \text{ }^\circ\text{C min}^{-1}$ from room temperature to $900 \text{ }^\circ\text{C}$ under flowing nitrogen.

UV-Vis-NIR Diffuse Reflectance Spectroscopy

The UV-Vis-NIR diffuse reflection data were collected on a PerkinElmer Lambda-1050 UV/vis/NIR spectrophotometer. A whiteboard provided by the merchant was used as a reference (100% reflectance) in the range from 220 nm to 800 nm.

Infrared Spectroscopy

Infrared spectrum was measured on a Nicolet iS50FT-IR spectrometer with KBr pellets as a standard in the range of 4000~400 cm^{-1} . The mixture of **1** and dried KBr (mass ratio = 1:100) was ground thoroughly in an agate mortar, and then pressed into a thin slice for measurement.

Computational Methods

The first-principles calculations for **1** were performed by CASTEP⁵ on a plane-wave pseudopotential total energy package based density functional theory (DFT).⁶ The functional developed by Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA)⁷⁻⁸ form was adopted to describe the exchange-correlation energy. The ultrasoft pseudopotentials were used to model the effective interaction between atom cores and valence electrons. H 1s¹, C 2s²2p², N 2s²2p³, O 2s²2p⁴, F 2s²2p⁵ and Si 3s²3p² electrons were treated as valence electrons. The kinetic energy cutoff of 380 eV (for **1**), 310 eV (for melamine) and dense $2 \times 1 \times 1$ (for **1**), $1 \times 2 \times 2$ (for melamine) Monkhorst-Pack⁹ k-point meshes in the Brillouin zones were chosen. The linear optical properties were examined based on the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part of dielectric function ε_2 can be calculated based on the electronic structures and the real part is obtained by the Kramers-Kronig transformation, accordingly the refractive indices and the birefringence (Δn) can be calculated. The frequency-dependent refractive indices were calculated to demonstrate the validity of birefringence measurements.

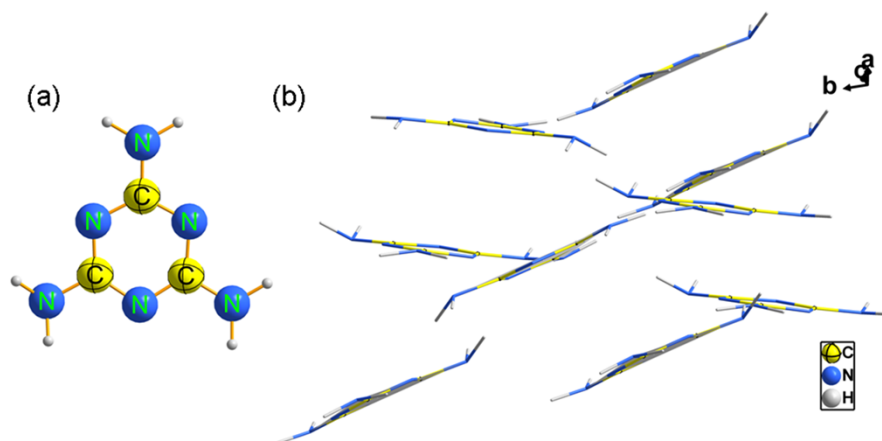


Figure S1. (a) One $C_3N_6H_6$ molecule. (b) Arrangement of $C_3N_6H_6$ molecules in the melamine.

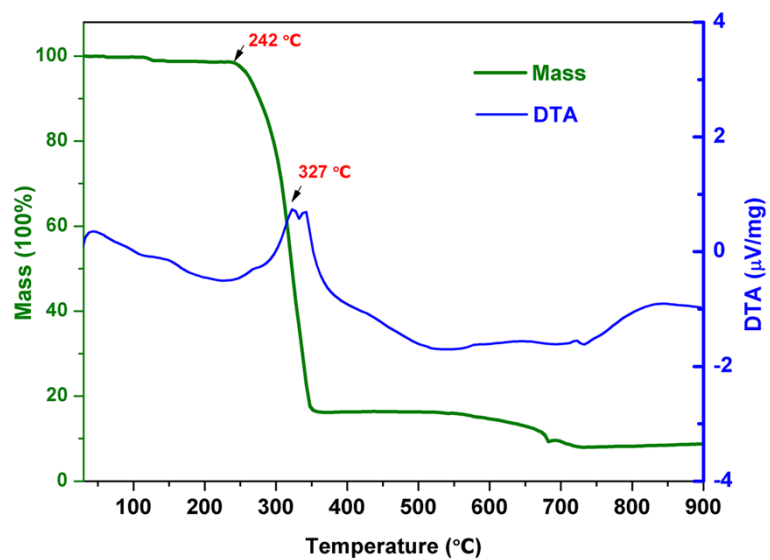


Figure S2. Thermal stability analysis for **1**.

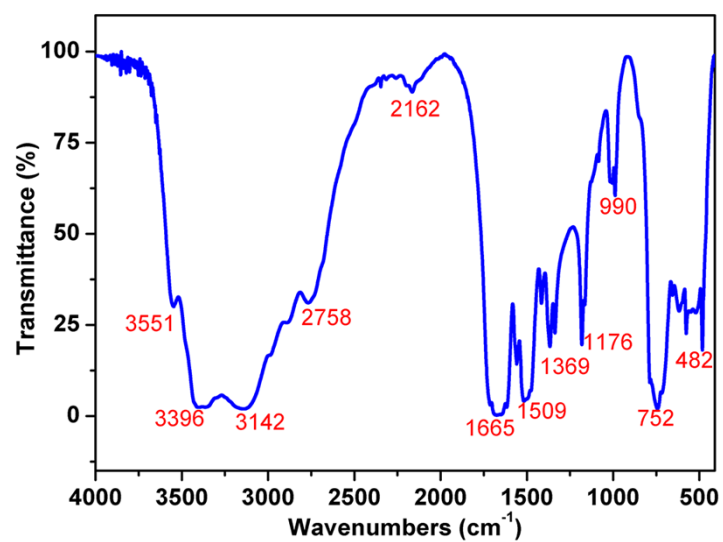


Figure S3. Infrared spectrum of 1.

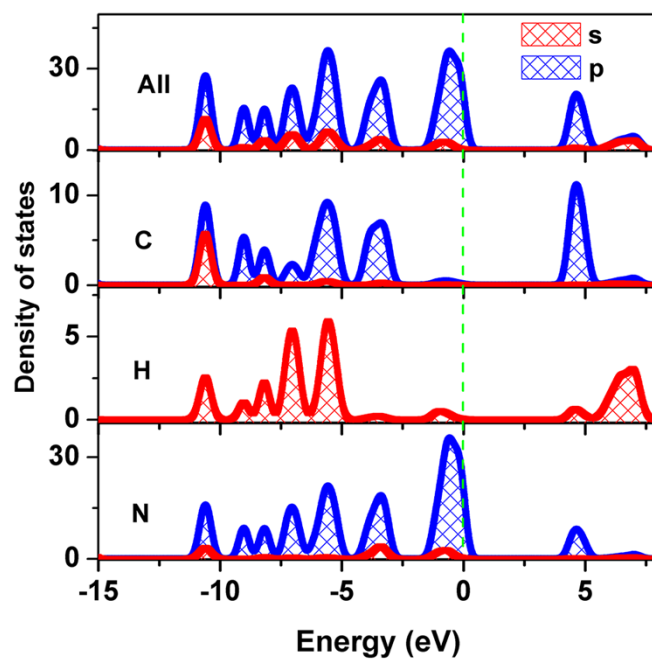


Figure S4. Density of states for melamine.

Table S1. Crystal Data and Structural Refinement for (C₃N₆H₇)₂SiF₆·H₂O.

Empirical formula	C ₆ H ₁₆ N ₁₂ OSiF ₆
Formula weight	414.40
Temperature/K	297.14(10)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	7.7315(3)
<i>b</i> /Å	10.8592(3)
<i>c</i> /Å	17.9424(6)
α /°	90
β /°	91.245(3)
γ /°	90
Volume/Å ³	1506.05(9)
<i>Z</i>	4
ρ_{calc} g/cm ³	1.828
μ /mm ⁻¹	0.256
<i>F</i> (000)	848.0
Crystal size/mm ³	0.12 × 0.11 × 0.1
Radiation	Mo K α (λ = 0.71073 Å)
2 Θ range for data collection/°	4.384 to 58.662
Index ranges	-9 ≤ <i>h</i> ≤ 9, -13 ≤ <i>k</i> ≤ 12, -22 ≤ <i>l</i> ≤ 19
Reflections collected	10674
Independent reflections	3275 [<i>R</i> _{int} = 0.0190, <i>R</i> _{sigma} = 0.0222]
Data/restraints/parameters	3275/5/251
Goodness-of-fit on <i>F</i> ²	1.061
Final <i>R</i> indexes [<i>I</i> >= 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0416, <i>wR</i> ₂ = 0.1134
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0512, <i>wR</i> ₂ = 0.1205

Table S2. The Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $(\text{C}_3\text{N}_6\text{H}_7)_2\text{SiF}_6 \cdot \text{H}_2\text{O}$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Si1	5342.1(6)	4975.8(4)	7581.4(3)	27.15(16)
F1	4306.4(19)	3725.2(11)	7890.7(9)	58.0(4)
F2	5378(2)	4350.8(14)	6732.3(8)	62.4(4)
F3	3425.9(16)	5631.6(11)	7384.8(8)	50.2(4)
F4	6340.6(19)	6237.9(13)	7283.7(8)	59.9(4)
F5	5317(2)	5563.2(12)	8445.2(7)	53.9(4)
F6	7237.1(16)	4311.7(14)	7774.2(9)	64.9(5)
O1	1204(2)	3212.9(15)	7195.0(10)	52.3(5)
N1	4333(2)	-2386.5(14)	5975.4(9)	36.3(4)
N2	2959(2)	-801.4(13)	5353.0(9)	27.9(3)
N3	1744(2)	866.0(14)	4760.5(9)	32.3(4)
N4	3546(2)	1282.3(13)	5745.4(8)	26.6(3)
N5	5483(2)	1589.9(14)	6716.2(9)	33.1(4)
N6	4867.7(17)	-388.8(14)	6334.7(8)	30.3(4)
C1	4036(2)	-1195.7(16)	5884.5(10)	27.3(4)
C2	2767(2)	440.5(15)	5301.0(10)	25.0(4)
C3	4625(2)	846.9(16)	6263.4(10)	25.2(4)
N7	8716(2)	2563.7(13)	5692.5(9)	36.2(4)
N8	9457(2)	4479.1(13)	6122.2(9)	27.3(3)
N9	10303(2)	6369.2(15)	6549.3(9)	34.6(4)
N10	8360.5(19)	6268.4(13)	5559.9(8)	25.9(3)
N11	6574(2)	6019.6(14)	4552.0(9)	34.0(4)
N12	7583.6(19)	4252.3(13)	5088.3(8)	25.6(3)
C4	8558(2)	3765.1(15)	5626.2(10)	25.2(4)
C5	9350(2)	5725.3(15)	6073.1(9)	25.0(4)
C6	7518(2)	5502.7(15)	5082.7(10)	24.8(4)

Table S3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $(\text{C}_3\text{N}_6\text{H}_7)_2\text{SiF}_6 \cdot \text{H}_2\text{O}$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	31.2(3)	21.9(3)	27.8(3)	-3.83(18)	-12.2(2)	0.89(18)
F1	68.7(9)	28.2(6)	76.0(10)	14.5(6)	-22.9(8)	-11.7(6)
F2	71.7(10)	75.4(10)	39.3(8)	-24.0(7)	-19.7(7)	9.2(8)
F3	39.4(7)	37.8(7)	72.6(10)	7.1(6)	-17.1(6)	9.0(5)
F4	61.3(9)	55.5(9)	62.6(10)	12.5(7)	-5.0(7)	-25.0(7)
F5	78.9(10)	47.2(8)	35.3(7)	-12.5(6)	-5.4(7)	-0.4(7)
F6	46.6(8)	70.4(10)	75.9(11)	-24.4(8)	-35.0(7)	23.1(7)
O1	58.7(11)	36.0(9)	60.9(11)	15.8(7)	-30.8(9)	-12.2(7)
N1	47.1(10)	23.2(8)	38.1(9)	2.1(6)	-10.7(8)	5.6(7)
N2	32.3(8)	22.8(7)	28.2(8)	-0.7(6)	-6.8(6)	1.6(6)
N3	37.4(9)	24.6(8)	34.2(9)	-0.1(6)	-13.4(7)	2.1(6)
N4	31.3(8)	21.2(7)	27.0(8)	-1.1(6)	-4.4(6)	1.0(6)
N5	37.3(9)	28.6(8)	32.7(9)	-3.7(6)	-12.3(7)	0.8(6)
N6	34.1(9)	26.0(8)	30.4(9)	1.5(6)	-10.6(7)	3.0(6)
C1	30.4(9)	25.3(9)	26.3(9)	-1.1(7)	-0.5(7)	1.3(7)
C2	24.7(9)	23.9(8)	26.3(9)	-1.2(7)	0.0(7)	1.4(6)
C3	27.4(9)	26.3(8)	21.8(9)	-0.4(6)	-1.0(7)	1.0(7)
N7	52.4(11)	21.3(8)	34.1(9)	2.7(6)	-14.9(8)	-1.6(7)
N8	33.2(9)	22.9(7)	25.4(8)	1.3(6)	-7.6(7)	1.4(6)
N9	41.8(10)	28.6(8)	32.6(9)	-3.8(6)	-14.0(7)	-0.7(6)
N10	28.5(8)	21.5(7)	27.5(8)	-2.5(6)	-5.9(6)	-0.4(5)
N11	40.1(9)	22.7(8)	38.4(9)	-0.6(6)	-18.9(7)	1.3(6)
N12	29.4(8)	21.9(7)	25.2(8)	-0.9(5)	-6.3(6)	-1.2(6)
C4	28.6(9)	23.5(8)	23.3(9)	0.2(6)	0.1(7)	-0.8(6)
C5	26.9(9)	25.9(9)	22.0(9)	-2.4(6)	-0.9(7)	0.1(6)
C6	24.1(9)	24.2(8)	26.2(9)	0.0(6)	-0.7(7)	-0.2(6)

Table S4. Bond Lengths for (C₃N₆H₇)₂SiF₆·H₂O.

Atom Atom Length/Å			Atom Atom Length/Å		
Si1	F1	1.6771(13)	N5	C3	1.314(2)
Si1	F2	1.6686(14)	N6	C1	1.346(2)
Si1	F3	1.6745(12)	N6	C3	1.360(2)
Si1	F4	1.6666(13)	N7	C4	1.316(2)
Si1	F5	1.6766(13)	N8	C4	1.360(2)
Si1	F6	1.6626(12)	N8	C5	1.359(2)
N1	C1	1.323(2)	N9	C5	1.317(2)
N2	C1	1.323(2)	N10	C5	1.323(2)
N2	C2	1.360(2)	N10	C6	1.351(2)
N3	C2	1.321(2)	N11	C6	1.313(2)
N4	C2	1.346(2)	N12	C4	1.322(2)
N4	C3	1.323(2)	N12	C6	1.359(2)

Table S5. Bond Angles for (C₃N₆H₇)₂SiF₆·H₂O.

Atom Atom Atom Angle/°				Atom Atom Atom Angle/°			
F2	Si1	F1	89.44(8)	N2	C1	N6	120.45(16)
F2	Si1	F3	90.74(8)	N3	C2	N2	117.38(16)
F2	Si1	F5	178.33(8)	N3	C2	N4	116.74(16)
F3	Si1	F1	89.28(7)	N4	C2	N2	125.87(16)
F3	Si1	F5	90.29(8)	N4	C3	N6	120.14(15)
F4	Si1	F1	178.75(8)	N5	C3	N4	121.13(16)
F4	Si1	F2	91.43(9)	N5	C3	N6	118.73(16)
F4	Si1	F3	89.81(7)	C5	N8	C4	119.74(15)
F4	Si1	F5	89.89(8)	C5	N10	C6	115.50(15)
F5	Si1	F1	89.25(8)	C4	N12	C6	115.22(15)
F6	Si1	F1	90.28(8)	N7	C4	N8	117.47(16)
F6	Si1	F2	88.94(8)	N7	C4	N12	120.88(16)
F6	Si1	F3	179.45(7)	N12	C4	N8	121.64(15)
F6	Si1	F4	90.64(8)	N9	C5	N8	117.03(16)
F6	Si1	F5	90.03(7)	N9	C5	N10	121.45(16)
C1	N2	C2	115.87(15)	N10	C5	N8	121.50(16)
C3	N4	C2	116.14(15)	N10	C6	N12	126.35(16)
C1	N6	C3	121.51(14)	N11	C6	N10	116.71(16)
N1	C1	N2	120.66(17)	N11	C6	N12	116.92(16)
N1	C1	N6	118.88(17)				

Table S6. Hydrogen Bonds for (C₃N₆H₇)₂SiF₆·H₂O.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1C	F1	0.870(17)	1.874(18)	2.737(2)	171(3)
N6	H6	F6 ¹⁾	0.791(9)	1.979(11)	2.7418(9)	162(2)
N7	H7B	F5 ¹⁾	0.86	2.07	2.761(2)	137.0
N8	H8	O1 ²⁾	0.90(3)	1.81(3)	2.703(2)	176(2)
N9	H9A	F1 ³⁾	0.86	2.01	2.763(2)	145.3
N11	H11B	F2 ⁴⁾	0.86	2.02	2.756(2)	142.5

¹⁾3/2-X,-1/2+Y,3/2-Z; ²⁾1+X,+Y,+Z; ³⁾3/2-X,1/2+Y,3/2-Z; ⁴⁾1-X,1-Y,1-Z

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