

Supporting Information

A novel 0D germanium-based organic-inorganic hybrid material (C₁₂H₂₈N)GeCl₃ showing reversible phase transition, dielectric anomaly and SHG response

Jie Zhou,¹ Binyi Tong,¹ Zhirong Zhong,¹ An Duan,¹ Yong Ai,¹ Lin

Zhou,^{*,1} Zhenhong Wei,^{*,1} Hu Cai^{*,1,2}

¹ School of Chemistry and Chemical Engineering, Nanchang University,

Nanchang, 330031, P. R. China

² State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P. R.

China

*Corresponding Author(s): weizh@ncu.edu.cn

Measurement Methods

Single-crystal and powder X-ray crystallography.

X-ray single-crystal diffraction experiments were performed utilizing a Rigaku Saturn 924 diffractometer, outfitted with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). X-ray diffraction (XRD) analyses were executed employing a PANalytical X'Pert3 diffractometer, equipped with a Cu K α X-ray source ($\lambda = 1.5418 \text{ \AA}$, 40 kV, 150 mA), with a scan rate set at $10^\circ \text{ min}^{-1}$ for the measurements.

Thermal analyses

Differential scanning calorimetry (DSC) measurements were performed with a NETZSCH DSC 200F3 instrument. Crystalline samples (7.8mg) underwent both heating and cooling processes at a consistent rate of 20 K min^{-1} under aluminum crucibles and nitrogen atmosphere.

SHG and dielectric measurements

The second harmonic generation (SHG) was examined using INSTEC instruments. The reference material KDP was ground and sieved under the same conditions as the target sample to ensure a consistent particle size distribution (80–150 μm). Complex dielectric permittivities were assessed utilizing the DMS-1000 dielectric temperature spectrum measuring system. Silver conductive paste was utilized to coat the surfaces of the samples, serving dual roles as the top and bottom electrodes.

IR measurements.

The Fourier transform infrared (FTIR) spectra were obtained using a Bruker Alpha II instrument. The sample was measured using the KBr pellet method at a ratio of 100:1.

Experimental

During the preparation process, experimental reagents triisobutylamine, GeO₂, and hydroiodic acid were purchased and used directly without additional purification.

Synthesis of (C₁₂H₂₈N)GeCl₃ (1): Add 5 mL of hypophosphite (55%, 1.5 g) and GeO₂ (2.0 mmol, 0.2 g) sequentially to 10 mL of concentrated HCl (45%, 1.8 g), stir evenly, and then heat. After the solution is clear, add triisobutylamine (2.0 mmol, 0.37 g) and continue stirring for 30 minutes. The clear solution obtained is slowly cooled to room

temperature and slowly evaporated to obtain colorless needle shaped crystals. The crystals are separated by filtration and dried in a vacuum drying oven. Yield: 0.56g, 76.71%. Anal. calculated for $(C_{12}H_{28}N)GeCl_3$: C, 39.35; H, 7.73; N, 3.83 Found: C, 39.28; H, 7.81; N, 3.79. IR (KBr, cm^{-1}): 3238(m), 2969(vs), 2872(vs), 2360(w), 1457(m), 1377(vs), 1236(w), 1103(m), 998(w), 883(w), 867(w), 760(m), 530(vs), 403(vs).

Computational Methods

The dipole moment calculation was performed based on density functional theory (DFT). DFT calculations were carried out using Gaussian 16 (EM64W-G16RevA.03) with the B3LYP functional combined with the aug-cc-pVDZ basis set.

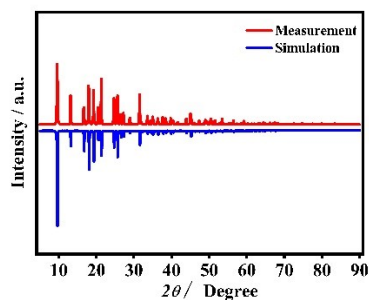


Fig. S1. Powder X-ray diffractograms of compounds **1**.

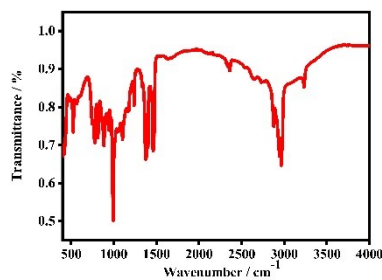


Fig. S2. Infrared spectra of solid compounds **1** in KBr particles recorded at room temperature.

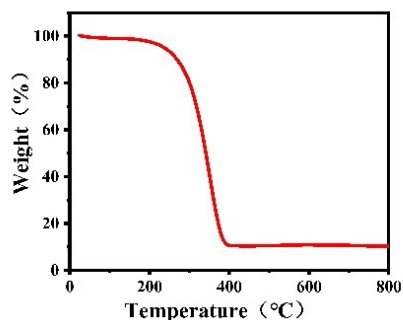


Fig. S3 TGA curve of compound **1**.

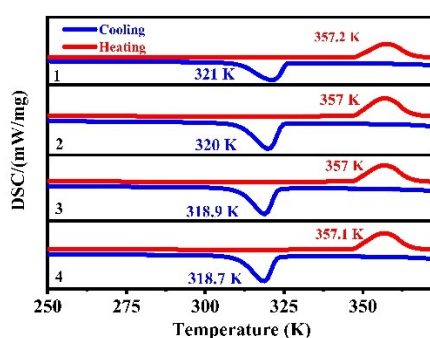


Fig. S4 Four consecutive DSC measurements of compound **1**.

Table S1. Crystal data and structure refinement for **1** at 293 K.

Empirical formula	$C_{12}H_{28}Cl_3GeN$
Formula weight	365.29
Temperature/K	293(2)
Crystal system	hexagonal
Space group	$P6_3$
$a/\text{\AA}$	10.5973(4)
$b/\text{\AA}$	10.5973(4)
$c/\text{\AA}$	9.8138(7)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	120
Volume/ \AA^3	954.46(10)
Z	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.271
μ/mm^{-1}	2.009
F(000)	380.0
Crystal size/ mm^3	$0.02 \times 0.01 \times 0.01$
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	6.078 to 61.528
Index ranges	$-15 \leq h \leq 12, -14 \leq k \leq 12, -12 \leq l \leq 10$
Reflections collected	4767
Independent reflections	1483 [$R_{\text{int}} = 0.0207, R_{\text{sigma}} = 0.0231$]
Data/restraints/parameters	1483/1/54
Goodness-of-fit on F^2	0.912
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0449, wR_2 = 0.1215$
Final R indexes [all data]	$R_1 = 0.0671, wR_2 = 0.1345$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.23/-0.25

Flack parameter	0.022(15)
-----------------	-----------

Table S2. Bond Lengths for **1** at 293 K.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Ge01	Cl02	2.2776(17)		N003	C005 ²	1.511(4)
Ge01	Cl02 ¹	2.2776(17)		C004	C005	1.519(6)
Ge01	Cl02 ²	2.2776(17)		C004	C006	1.540(7)
N003	C005	1.511(4)		C004	C007	1.472(9)
N003	C005 ¹	1.511(4)				

Table S3. Bond Angles for **1** at 293 K.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cl02	Ge01	Cl02 ¹	96.10(7)		C005	N003	C005 ¹	110.9(3)
Cl02	Ge01	Cl02 ²	96.10(7)		C005	C004	C006	105.9(4)
Cl02 ¹	Ge01	Cl02 ²	96.10(7)		C007	C004	C005	113.3(5)
C005	N003	C005 ²	110.9(3)		C007	C004	C006	111.6(6)
C005 ²	N003	C005 ¹	110.9(3)		N003	C005	C004	114.4(4)

Table S4. Hydrogen bond lengths [Å] and bond angles [°] of **1** at 293 K.

D-H...A	D-H [Å]	H...A[Å]	D...A[Å]	D-H...A[°]
C005-H00B...Cl02	0.97	2.82	3.747(6)	161