Supporting Information

Ferroelectric Crystals with Naphthenic Hydrocarbon-Modified Carborane Vertices

Wenjing Guo, Xiao Sun, Wenkang Cheng, Guoyong Chen, Ying Wei, Zhenhong Wei*, and Hu Cai*

[*]Prof. Dr. Z.-H. Wei, Prof. Dr. H. Cai

School of Chemistry and Chemical Engineering,

Nanchang University

Nanchang City, 330031, P.R. China

E-mail: caihu@ncu.edu.cn; weizh@ncu.edu.cn

Table of contents

Experimental Procedures

Materials

o-Carborane and bromoalkane were purchased from Bidepharm and Admas. All solvents were distilled from appropriate drying agents under argon before use.

1,2-(1,3-Propanediyl)-*o*-carborane (**1**) and 1,2-(1,4-Hexanediyl)-*o*-carborane (**2**): In a dry, inert argon atmosphere, *o*-carborane (**2**): In (288 mg, 2 mmol) was dissolved in anhydrous tetrahydrofuran (THF) as the solvent. To this solution, *n*-butyllithium in *n*-hexane (1.60 M, 2.5 mL, 4 mmol) was added dropwise at 0°C. The reaction mixture was then brought to room temperature and stirred for 1 hour. After cooling again to 0°C, 1-bromo-3-chloropropane (314.8 mg, 2 mmol) or 1,4-dibromobutane (431.8 mg, 2 mmol) was gradually added, followed by stirring overnight at room temperature. The reaction progress was monitored by thin-layer chromatography (TLC). Upon completion, the reaction mixture was quenched with 20 mL of water and extracted with diethyl ether (3 × 20 mL). The organic layers were dried over anhydrous sodium sulfate. After solvent removal, the residue was subjected to column chromatography on silica gel (300–400 mesh) using *n*-hexane as the eluent, yielding **1** and **2** as white powders. **Yield**: ***1***: 213.4 mg (58%). Anal. calcd. for $C_5H_{16}B_{10}$:C, 32.60; H, 8.70; B, 58.7. Found: C, 32.50; H, 8.80; B, 58.60.; ***2***: 237.6 mg (60%). Anal. calcd. for $C_6H_{18}B_{10}$:C, 36.40; H, 9.10; B, 54.50. Found: C, 36.20; H, 9.20; B, 54.60.

Measurement Methods

Single-crystal and powder X-ray crystallography.

X-ray single-crystal diffraction experiments were performed on a Rigaku Saturn 924 diffractometer with Mo-Kα radiation (λ = 0.71073 Å). For X-ray diffraction (XRD) analysis, a PANalytical X'Pert3 diffractometer with a Cu Kα X-ray source (λ = 1.5418 Å, 40 kV, 150 mA) was used, and measurements were conducted at a scan rate of 10° min^{-1}. Supplementary crystallographic data for this study, assigned as Deposition Numbers **2400878** (for 1,2-(1,3-Propanediyl)-*o*-carborane) and **2400879** (for 1,2-(1,4-Hexanediyl)-*o*-carborane), are available without charge through the joint Access Structures service provided by the Cambridge Crystallographic Data Centre.

Thermal analyses.

Differential scanning calorimetry (DSC) analyses were conducted using a NETZSCH DSC 200F3 instrument. Crystalline samples were subjected to both heating and cooling cycles at a

constant rate of 20 K/min, with measurements performed in aluminum crucibles under a nitrogen atmosphere.

SHG and dielectric measurements.

The second harmonic generation (SHG) measurements were conducted using INSTEC instruments. Complex dielectric permittivity was measured with the DMS-1000 dielectric temperature spectrum measurement system. Silver conductive paste was applied to the surfaces of the samples to serve as both top and bottom electrodes.

Thin-Film Preparation

Indium tin oxide (ITO) glass substrates were subjected to a preliminary cleaning process prior to use. Crystalline samples **1** and **2** (each 20 mg) were dissolved in 300 μL of *n*-hexane. After cleaning, the ITO glass substrate was selected, and 20 μL of the solution was spin-coated onto its surface. The solvent was then allowed to evaporate gradually at room temperature, resulting in the formation of a polycrystalline thin film.

PFM characterization.

PFM measurements were performed using a piezoresponse force microscopy (PFM) system (Cypher ES by Oxford Instruments), equipped with a high-voltage package. PFM, an extension of atomic force microscopy (AFM), applies an AC drive voltage to a conductive tip to probe piezoelectric properties. In our experiments, we used conductive Pt/Ir-coated silicon probes (EFM, Nanoworld) with an approximate nominal spring constant of 2.8 nN/nm and a free-air resonance frequency of around 75 kHz. All PFM experiments were conducted in Dual Frequency Tracking mode, which enabled both high-resolution domain imaging and analysis of polarization switching behaviors.

IR measurements.

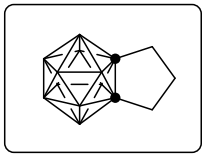
The powder was ground to a uniform particle size and its infrared spectrum was measured at room temperature. Fourier Transform Infrared (FTIR) spectra were recorded using a Bruker Alpha II instrument.

NMR measurements.

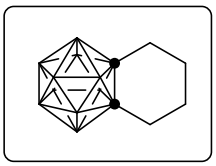
The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired using a Bruker Advance III 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C and 128 MHz for ^{11}B NMR). The samples were dissolved in either $CDCl_3$ or CD_3CN, with TMS serving as the internal reference

standard. The chemical shifts (δ) were measured in ppm and referenced to TMS (δ = 0) for ^{1}H, chloroform (δ = 77.0) for ^{13}C, and acetonitrile (δ = 118.26) for ^{13}C as internal standards. For ^{11}B and $^{11}B\{^{1}H\}$ NMR spectra, data were calibrated using external $BF_3 \cdot Et_2O$ as the reference compound.

Characterization data.



1: White solid, 77%; **^{1}H NMR (400 MHz, $CDCl_3$,** room temperature spectrum**)**: δ 2.51-2.48 (m, 4H), 2.45-2.39 (m, 2H); **$^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$,** room temperature spectrum**)**: δ 2.51-2.47 (m, 4H), 2.45-2.39 (m, 2H), 2.26 (s, 6H), 2.15 (s, 2H), 2.11 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$,** room temperature spectrum**)**: δ 83.81, 34.68, 32.02; **^{11}B NMR (128 MHz, $CDCl_3$,** room temperature spectrum**)**: δ -6.24 (s, 1B), -7.46 (s, 2B), -8.49 (s, 2B), -9.70 (s, 1B), -11.08 (s, 2B), -12.36 (s, 2B); **$^{11}B\{^{1}H\}$NMR (128 MHz, $CDCl_3$,** room temperature spectrum**)**: δ -6.79 (2B), -8.07 (2B), -8.99 (2B), -11.69 (4B).



2: White solid, 83%; **^{1}H NMR (400 MHz, $CDCl_3$,** room temperature spectrum**)**: δ 2.43 (m, 4H), 1.60-1.56 (m, 4H); **$^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$,** room temperature spectrum**)**: δ 2.42-2.39 (m, 4H), 2.30-2.26 (m, 2H), 2.19-2.01 (m, 8H), 1.58-1.48 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$,** room temperature spectrum**)**: δ 73.08, 32.74, 19.63; **^{11}B NMR (128 MHz, $CDCl_3$,** room temperature spectrum**)**: δ -5.19 – -6.34 (d, 2B), -8.93 – -10.22 (d, 1B), -10.91 – -12.28 (d, 2B); **$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$,** room temperature spectrum**)**: δ -5.79 (2B), -9.59 (6B), -11.65 (2B).

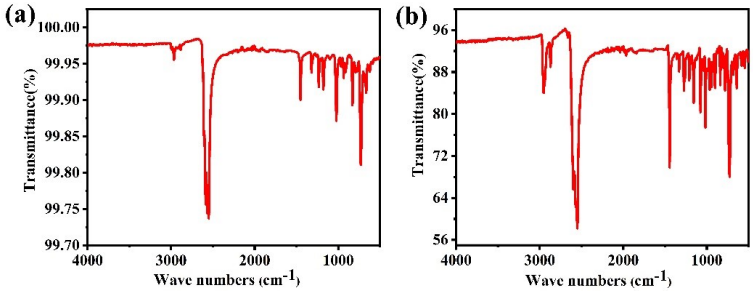
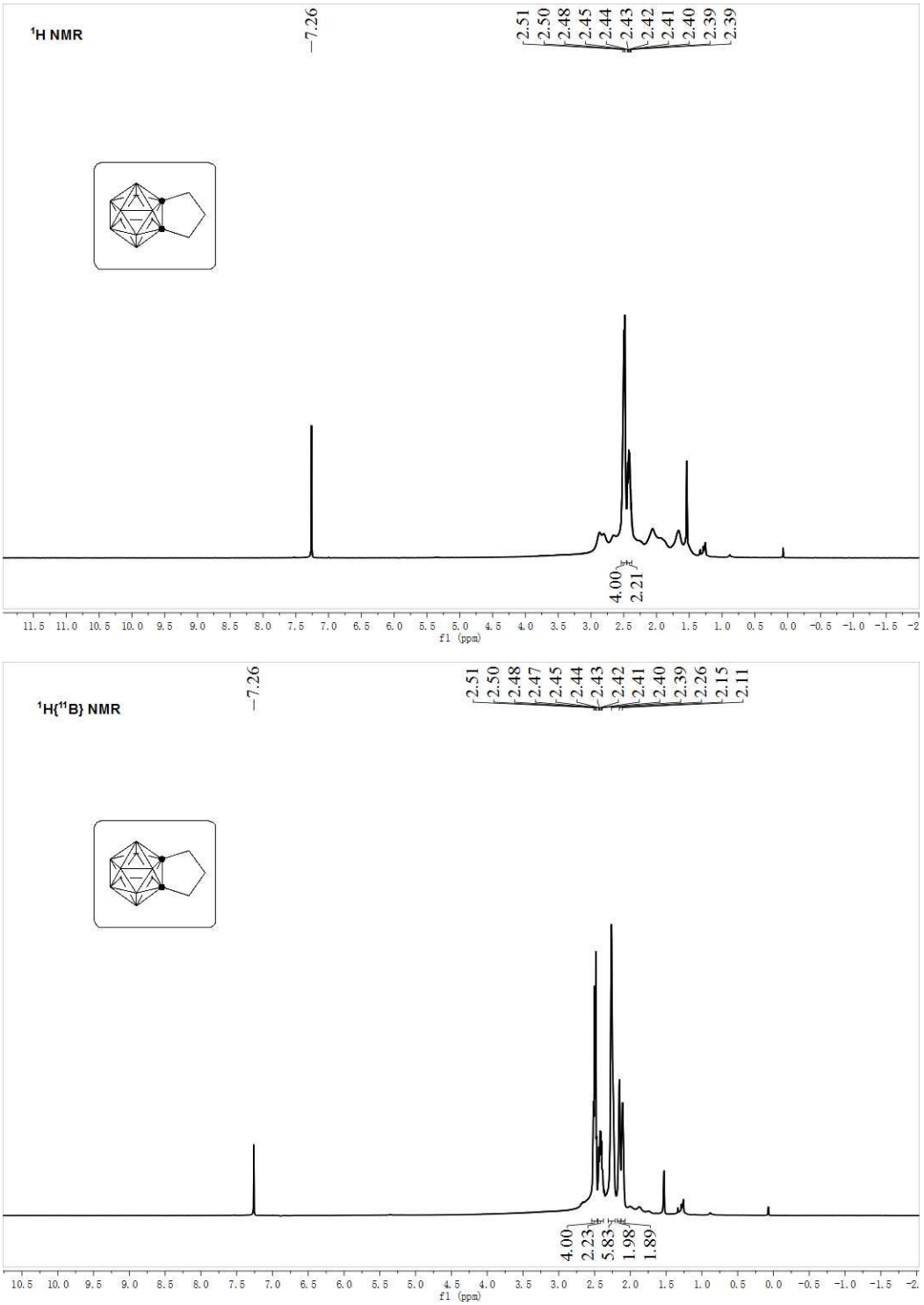
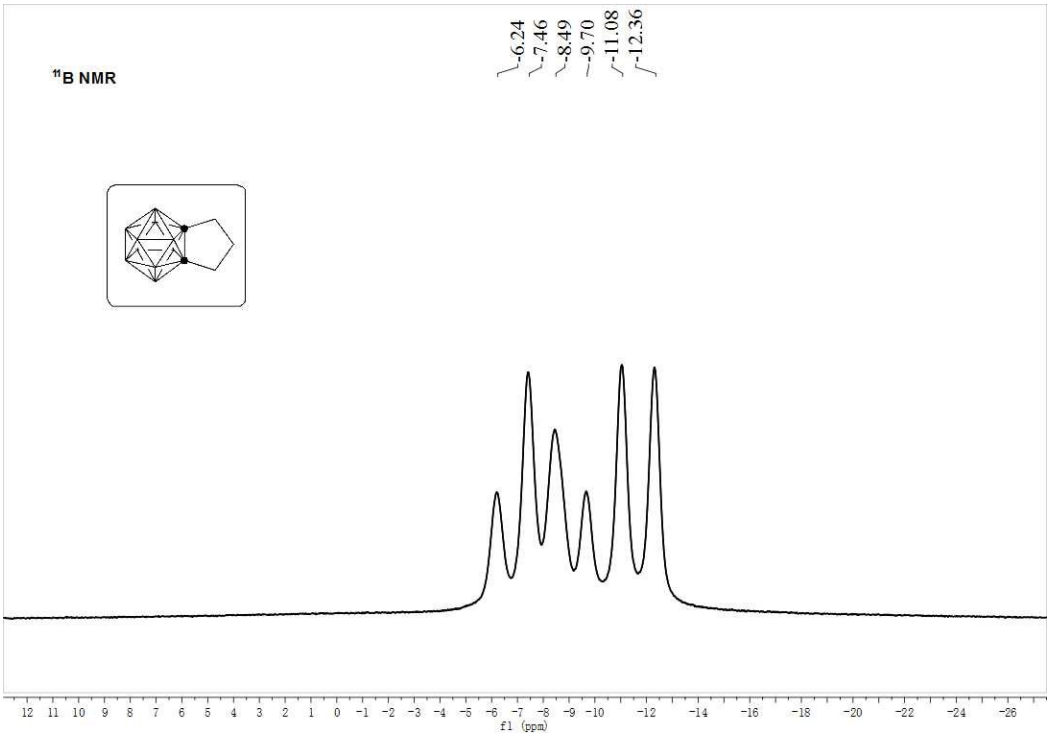
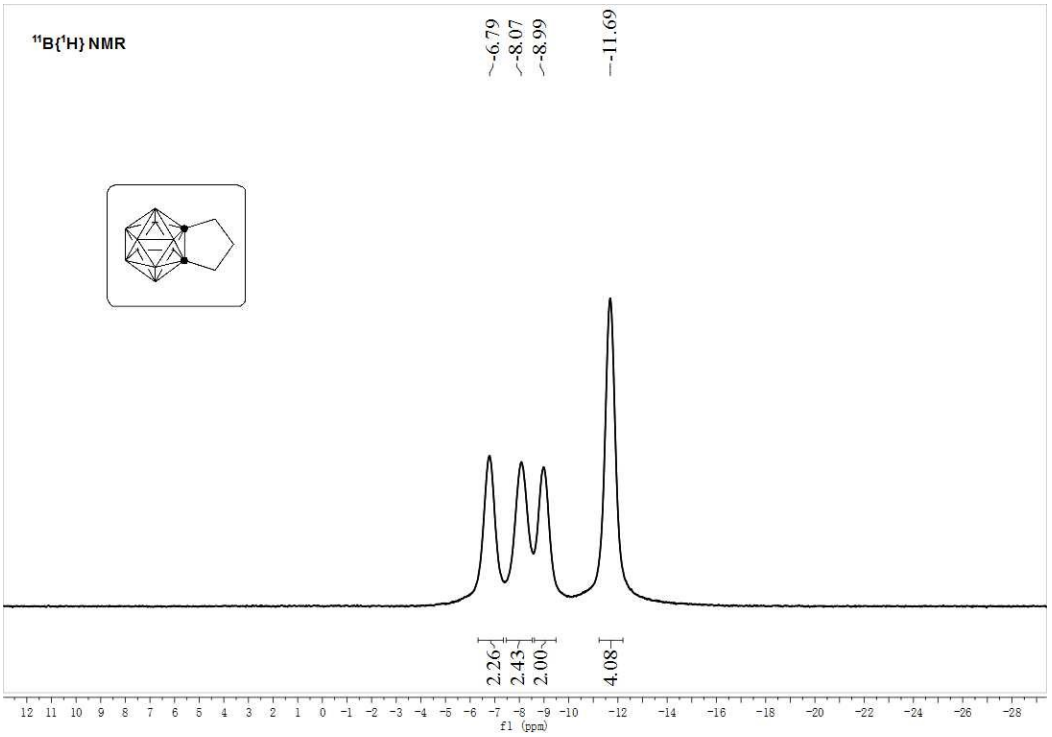


Figure S1. Experimental IR absorption spectra of **1** (a) and **2** (b)**.**




11B NMR
-6.24
-7.46
-8.49
-9.70
-11.08
-12.36
f1 (ppm)


11B{1H} NMR
-6.79
-8.07
-8.99
-11.69
2.26
2.43
2.00
4.08
f1 (ppm)

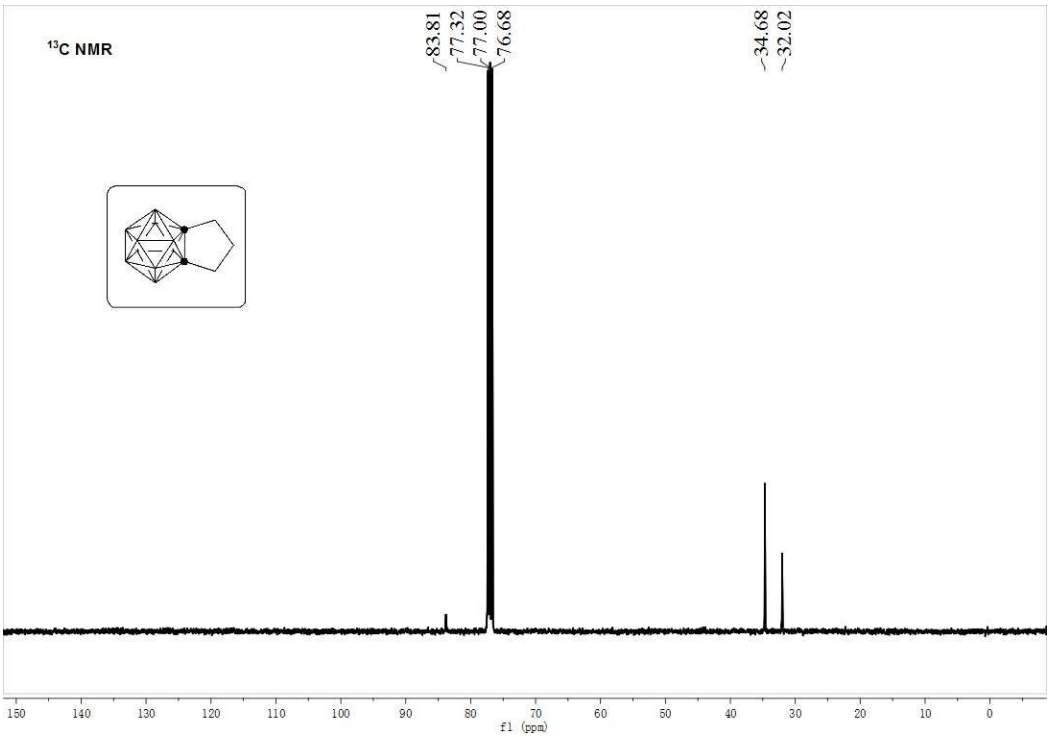
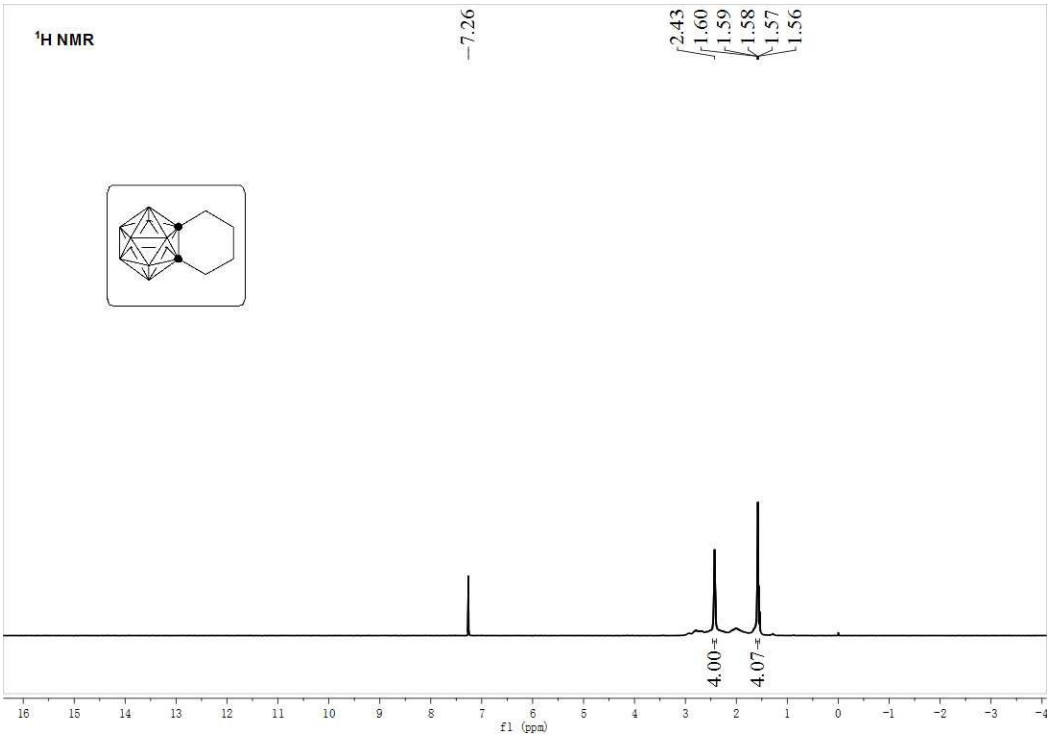
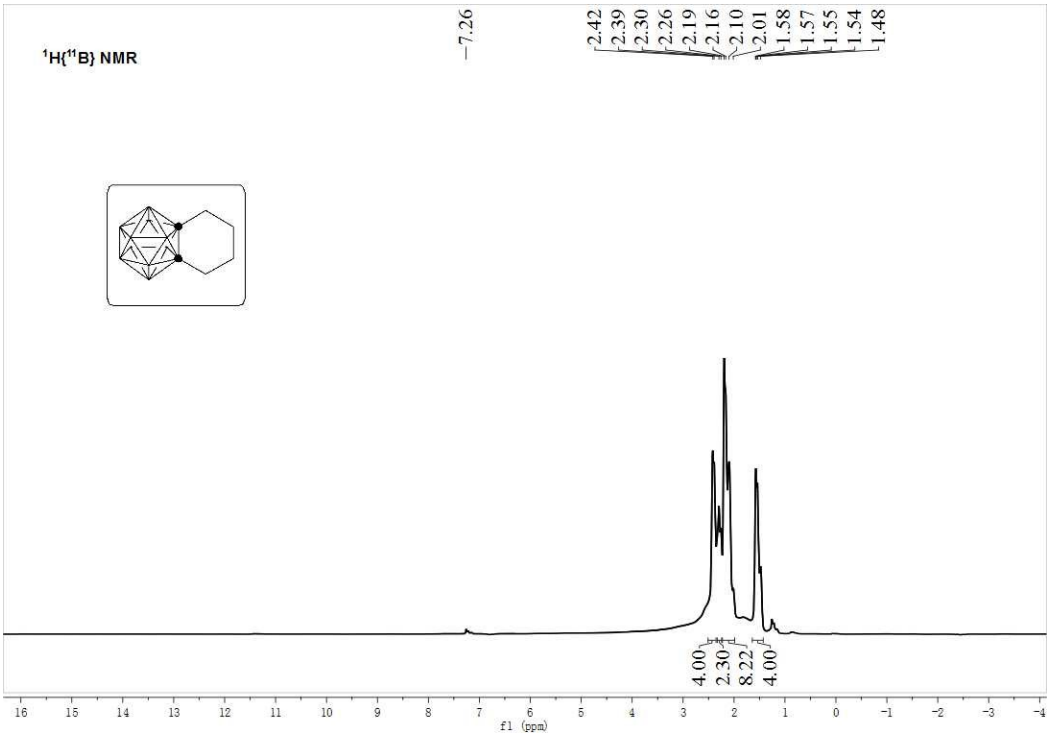
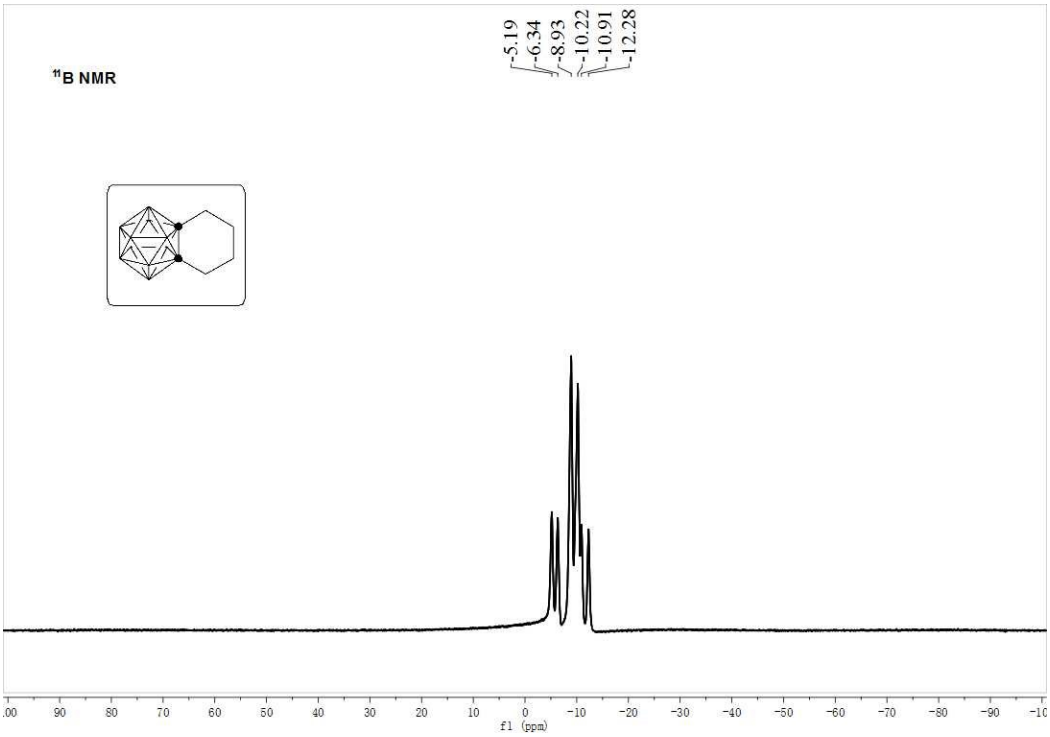


Figure S2. The ^{1}H NMR, $^{1}H\{B\}$ NMR, ^{11}B NMR, $^{11}B\{^{1}H\}$ NMR and ^{13}C NMR spectrum of **1** in $CDCl_3$.




$^{1}H\{^{11}B\}$ NMR
7.26
2.42
2.39
2.30
2.26
2.19
2.16
2.10
2.01
1.58
1.57
1.55
1.54
1.48
4.00
2.30
8.22
4.00
f1 (ppm)


^{11}B NMR
-5.19
-6.34
-8.93
-10.22
-10.91
-12.28
f1 (ppm)

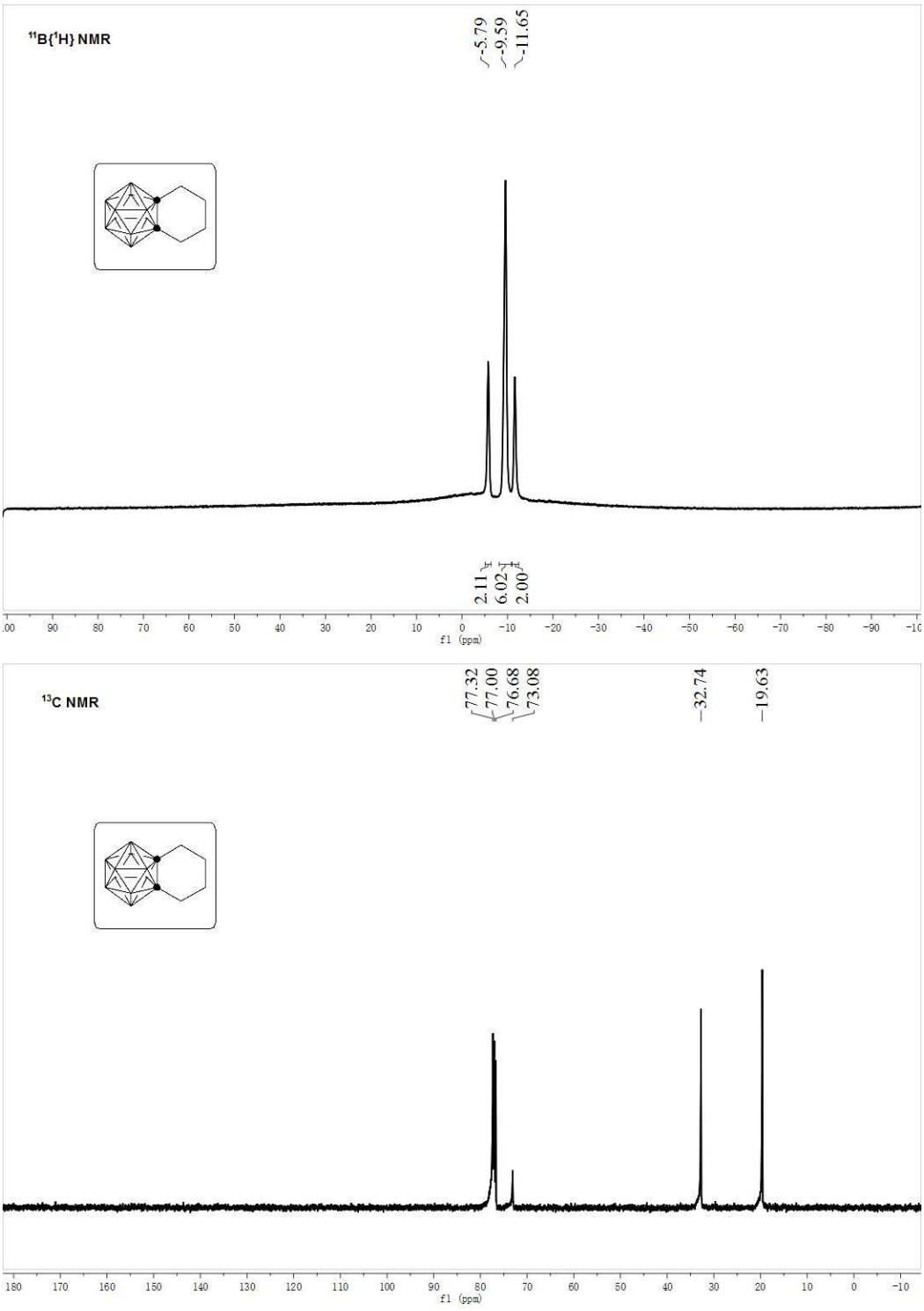


Figure S3. The ^{1}H NMR, $^{1}H\{B\}$ NMR, ^{11}B NMR, $^{11}B\{^{1}H\}$ NMR and ^{13}C NMR spectrum of **2** in $CDCl_3$.

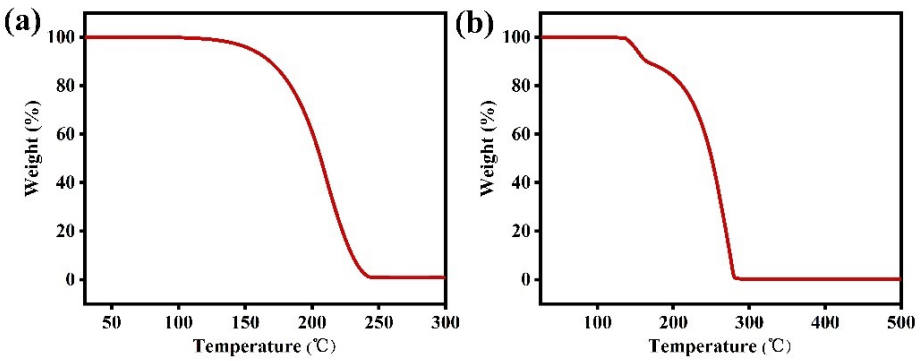


Figure S4. TGA of **1** (a) and **2** (b)**.**

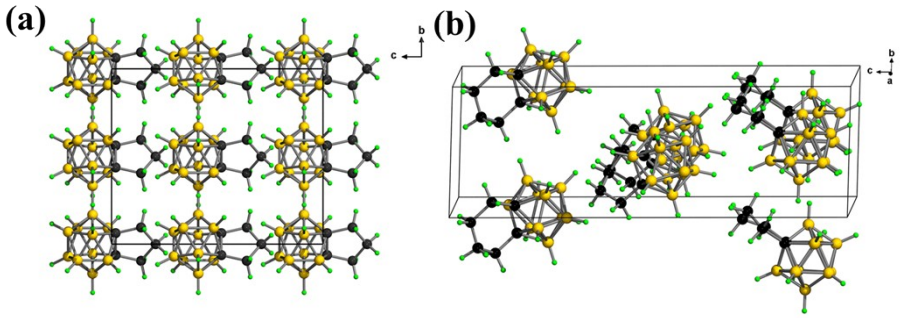


Figure S5. Crystal packing diagram of **1** (a) and **2** (b)**.**

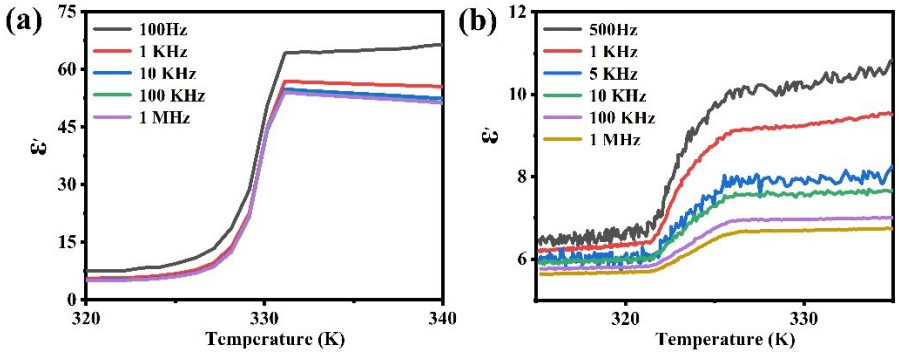


Figure S6. The temperature-dependent real part (ε') of the dielectric constant at different frequency for both **1** (a) and **2** (b)**.**

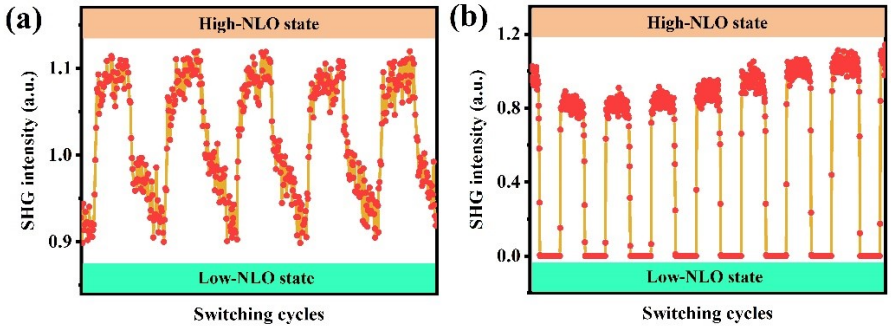


Figure S7. Switching SHG cycles of **1** (a) and **2** (b)**.**

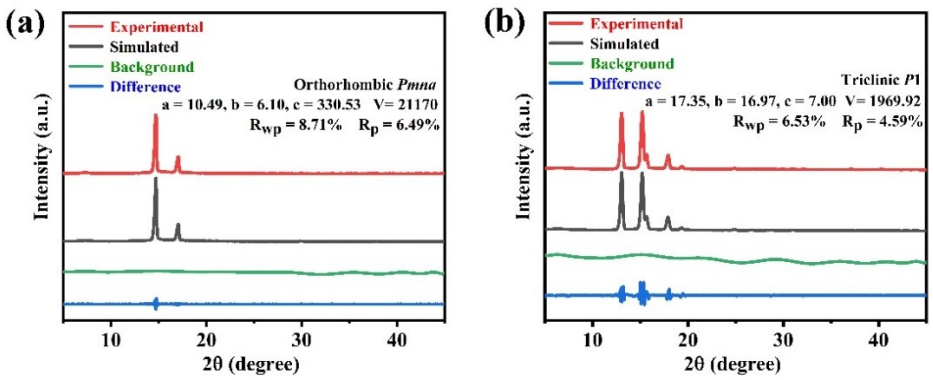


Figure S8. Pawley refinement of PXRD data of **1**−**2** collected at high temperature.

Table S1. Crystal data and structure refinement for **1**−**2**.

Formula	$C_5H_{16}B_{10}$	$C_6H_{18}B_{10}$
Temperature	296 K	296 K
Formula weight	184.28	198.30
Crystal system	orthorhombic	trigonal
Space group	*Aea* 2	$P\,3_1$
a (Å)	9.807(3)	7.2478(4)
b (Å)	9.951(4)	7.2478(4)
c (Å)	12.038(4)	20.608(2)
V(Å)^3	1174.8(7)	937.52(14)
Z	4	3
D_{calc} (g.cm^{-3})	1.042	1.054
F(000)	384.0	312.0
θ_{max}	27.193	30.945
μ(Mo Ka,mm^{-1})	0.045	0.047
Reflections collected	3170	7026

Unique reflections	1195 [$R_{(int)}$ = 0.0414]	1999 [$R_{(int)}$ = 0.0667]
No. of variables	69	145
Final R indices ($I \geq 2\sigma$)	R_1 = 0.0737, wR_2 = 0.1985	R_1 = 0.0704, wR_2 = 0.1676
R indices (all data)	R_1 = 0.1136, wR_2 = 0.2338	R_1 = 0.1258, wR_2 = 0.1899
Goodness-of-fit	1.037	0.944