Supplementary Material (ESI) for Dalton Transactions

Supporting information

The First Ferroelectric Templated Borate: $[Ni(en)_2pip][B_5O_6(OH)_4]_2$

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Experimental Section

Synthesis: **GDUT-4** was synthesized by refluxing H_3BO_3, water and triethylenetriamine. A standard reaction was typically 1.00 g H_3BO_3 and 0.36 g $NiCl_2{\cdot}6H_2O$ was mixed together in a 30 ml Teflon–lined bomb. Water (0.40mL) followed by triethylenetramine (0.20 mL) was added to the mixture drop by drop. The sealed bomb was heated at 200°C for 1 day and then allowed to slowly cool to room temperature. Large purple block crystals were recovered by filtration, washed with distilled water and dried in air. The yield of $[Ni(en)_2pip][B_5O_6(OH)_4]_2$ (denoted as **GDUT-4**) is very high (almost 60% based on $NiCl_2{\cdot}6H_2O$).

Crystal data for **GDUT-4**: $C_8H_{34}B_{10}N_6NiO_{20}$, M_r = 701.18, monoclinic, C_2, a =14.4598(17), b = 11.7213(17), c = 8.5302(14) Å, β = 90.875(10)º, V = 1445.6(4) Å^3, Z = 2, ρ = 1.611 g cm^{-3}, F(000) =770, GOF = 1.098, A total of 2956 reflections were collected and 2579 are unique (R_{int} = 0.0373). $R1/wR2$ = 0.0686/0.1947 for 2579 reflections ($I > 2\sigma(I)$) and 205 parameters. The intensity data were collected on a Mercury CCD diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at room temperature. All absorption corrections were performed using the multi-scan program. The structure was solved by direct methods and refined by full-matrix least squares on F^2 with the SHELXTL-97 program package. All non-hydrogen atoms were refined anisotropically. CCDC-721173 for **GDUT-4** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

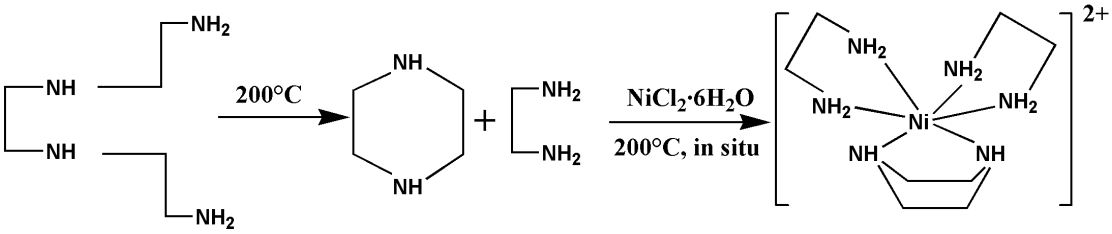
SHG Test : The powder second-harmonic generation test was carried out on the sample by the Kurtz and Perry method. Second-harmonic generation intensity data were obtained by placing a sieved (80–100 mesh) powder sample in an intense fundamental beam from a Q-switched Nd:YAG laser of wavelength 1064 nm. The output (λ = 532 nm) was filtered first to remove the multiplier and was then displayed on an oscilloscope. This procedure was then repeated using standard NLO material (microcrystalline KDP).

TGA Test: Thermogravimetric analysis was performed in a dry N_2 atmosphere from 30 to 1000 °C with a heating rate of 10 °C/min. As shown in Figure S5, the TG curve of **GDUT-4** showed that the compound was stable up to about 215°C. On further heating, a one-step weight

loss was observed. The weight loss between 215 and 720 °C corresponds to the removal of organic amines and the dehydration of hydroxyls (observed: 41.0%; expected: 39.7%).

IR spectrum (KBr pellet): The existence of BO_3 and BO_4 as well as organic groups can be confirmed by their characteristic bonds in the IR spectrum. The sharp peaks at 2940 and 2890cm^{-1} are characteristic of the stretching vibration of –CH_2– groups, the peak at 1610-1690cm^{-1} are characteristic of N-H bending, and peaks at 3340-3180cm^{-1} correspond to N-H stretching frequencies. The bands at about 1140-910cm^{-1} were attributed to the existence of trigonal boron (BO_3), the bands at about 1047 cm^{-1} and 983 cm^{-1} are attributed to the existence of tetrahedral boron (BO_4). (Figure S6).

Powder XRD: The experimental XRD pattern fits well with the stimulated pattern, indicating the phase-purity of **GDUT-4**. The difference in reflection intensities between the simulated and experimental patterns was due to the variation in preferred orientation for the powder sample (Figure S7).



Scheme 1: Decomposition of triethylenetramine and organic amines coordinated with Ni^{2+} cations to form complex cations *in situ* under boric reflux conditions.

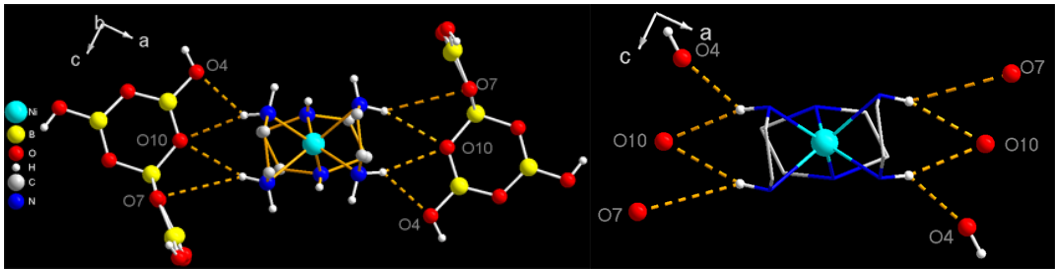


Figure S1: The guest-framework H-bonding interactions involved in the structure-directing effect appears to consist of two three-centre H-bonds for each polyanion through O4, O7 and O10 atoms, respectively.

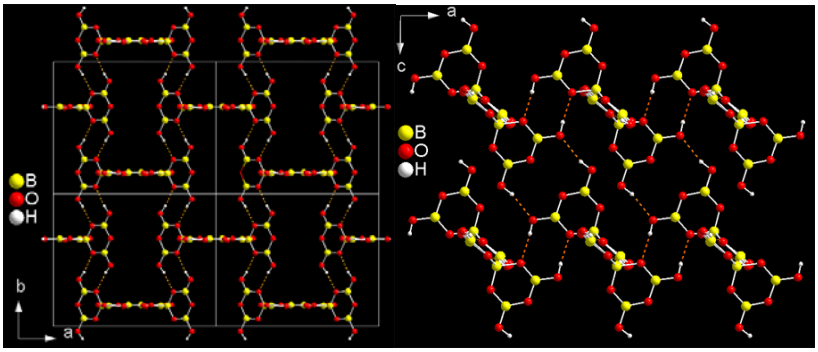


Figure S2:View of the hydrogen bonded architectures of **GDUT-4** in [001] and [010] directions, complex cations were omitted for clarity.

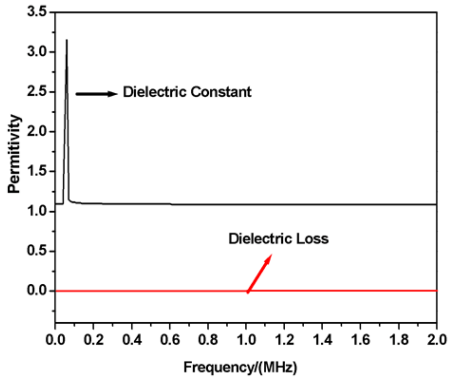


Figure S3: Frequency dependence of permittivity ((ε) = ε1(ω) – *i*ε2(ω)) of **GDUT-4** at room temperature.

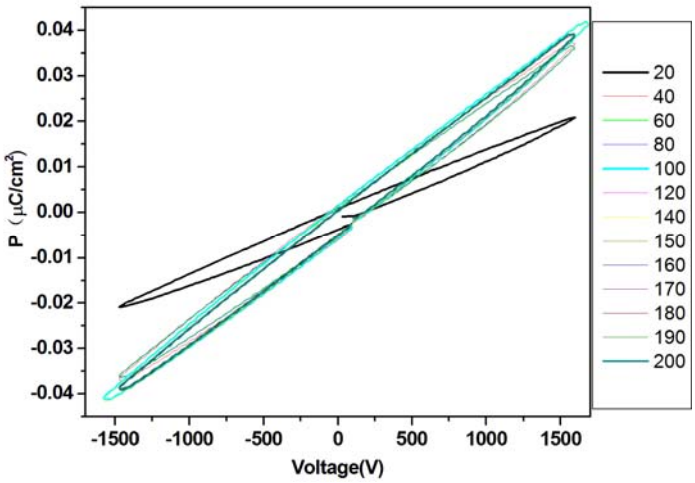


Figure S4: The electric hysteresis loops at various temperatures of a pellet obtained from a powdered sample of **GDUT-4**. Its Curie temperature is 200 °C .When temperature is more than 200 °C, electric hysteresis loop is disappeared.

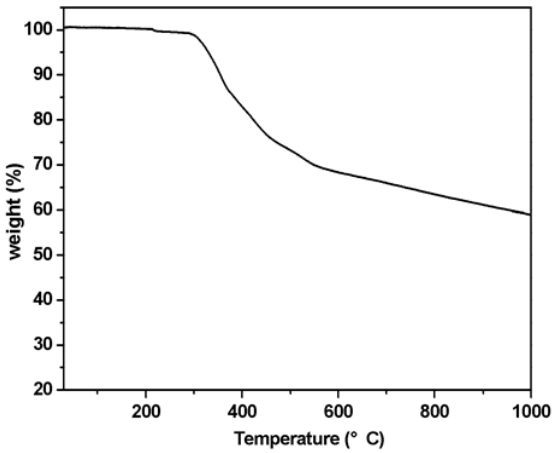


Figure S5: TG curve of **GDUT-4**

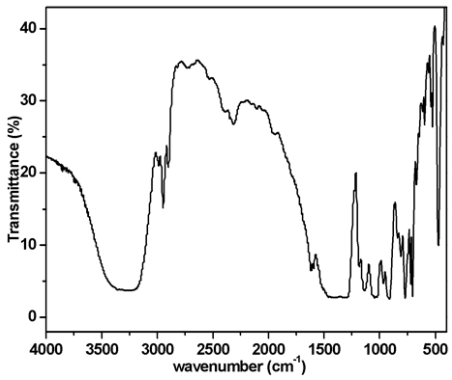


Figure S6: IR spectrum of **GDUT-4**.

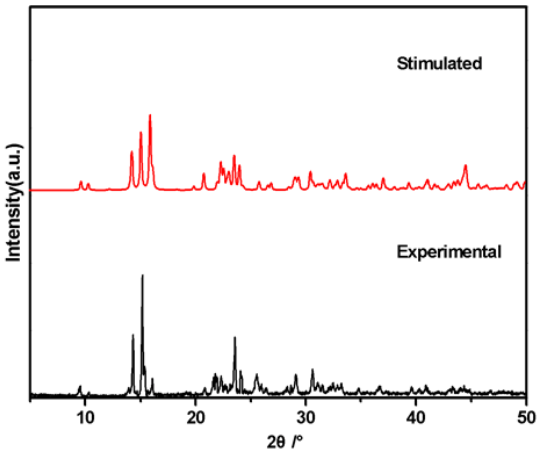


Figure S7: Experimental and simulated X-ray powder diffraction pattern of **GDUT-4**