Support information

Synthesis and Structure of QD-6: A Novel Aluminoborate Constructed From Unprecedented [B@Al_6O_{24}] and Polyborate Clusters

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Experimental Section

Synthesis: QD-6 was prepared under hydrothermal conditions from a mixture of Al(*i*-PrO)$_3$ or $AlCl_3 \cdot 6H_2O$, $NH_4B_5O_8 \cdot 4H_2O$, cyclopentylamine (CPA), pyridine and H_2O in a molar ratio of 1: 2.5: 5.5: 48: 61. Typically, 0.204 g of Al(*i*-PrO)$_3$ or 0.241 g of $AlCl_3 \cdot 6H_2O$ and 0.680 g of $NH_4B_5O_8 \cdot 4H_2O$ were dissolved in a mixed solution of 1.00 mL of H_2O and 5.00 mL of pyridine, and then 0.35 mL of CPA was slowly added under constant stirring. The resulting mixture was stirred at ambient temperature for 6h, then sealed in a 25-mL Teflon-lined autoclave and heated at 170°C for 13 days. The autoclave was cooled to room temperature, and colorless prismatic single crystals were separated from the solution by filtration, washed with distilled water and dried in air (46% yield based on Al). Strictly controlling the molar quantity of the organic amine (ca. 5.0-5.5 mmol) is crucial for the formation of QD-6; otherwise, a known polyborate $(NH_4)_2[B_{10}O_{14}(OH)_4] \cdot H_2O$[1] would be obtained when more or less amounts of CPA were used. Additionally, attempts to synthesize QD-6 from other aluminum sources such as Al_2O_3, $Al_2(SO_4)_3$ and $Al(NO_3)_3$, or by using boric acid as a boron source, were unsuccessful.

The experimental and simulated powder X-ray diffraction patterns are in good accordance with each other, indicating the phase purity of the sample (Fig. S4). IR (KBr pellet, cm^{-1}): 3454 cm^{-1} (OH), 1514 cm^{-1} (CPA), 1370 cm^{-1} (BO_3), 1275 cm^{-1} (AlO_6), 1063 cm^{-1} (BO_4) (Fig. S5).

Crystal data for **QD-6**: $C_{30}H_{159}N_{12}O_{153}B_{65}Al_{12}$, *M*r = 4163.10, trigonal, *R*-3 (No. 148). *a* =

23.7421(2) Å, c = 24.7699(3) Å, V = 12091.9(2) Å^3, Z = 3, ρ = 1.715 mg·cm^{-3}, λ = 0.71073 Å, μ(MoKα) = 0.219 mm^{-1}, F(000) = 6384. A total of 77316 reflections were collected in the range of 3.43° ≤ θ ≤ 28.28°, of which 6616 were unique (R_{int} = 0.0601) and 4606 with $I \geq 2\sigma(I)$ were collected for the analysis. The structure was solved and refined by full-matrix least squares on F^2 values (SHELXL-97). Non-H atoms were refined anisotropically. The final R_1 values were 0.0577 ($I \geq 2\sigma(I)$). The final $wR(F^2)$ values were 0.1692 ($I \geq 2\sigma(I)$). The final R_1 values were 0.0869 (all data). The final $wR(F^2)$ values were 0.1825 (all data). The goodness of fit on F^2 was 1.085. CCDC 803658 for **QD-6** 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.

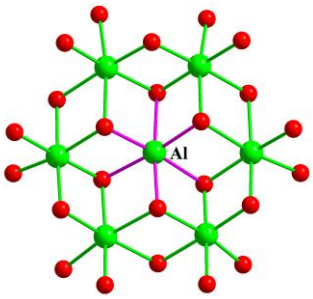

Figure S1. The $[Al_7O_{24}]$ cluster in PKU-8.

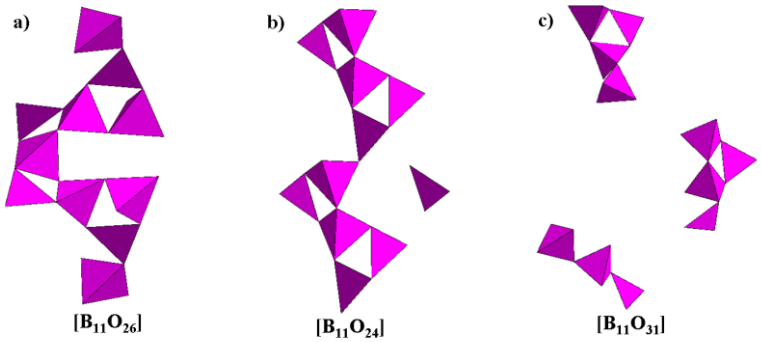

Figure S2. Comparison of the undecane borate *FBBs* observed in $Mg_3[B_{11}O_{15}(OH)_9]$ (a) $Sr_2B_{11}O_{16}(OH)_5\cdot(H_2O)$ (b) and $Pb_6B_{11}O_{18}(OH)_9$ (c).

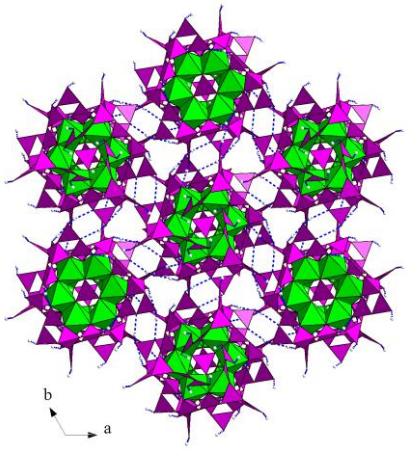

Figure S3. A projection of the structure of QD-6 along the *c*-axis. AlO_6, green octahedra, BO4 and BO3, purple.

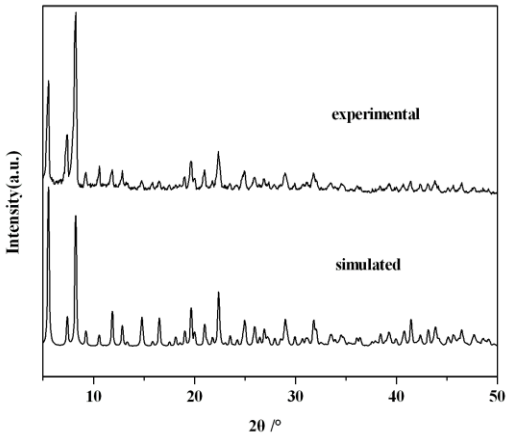

Figure S4. The XRD patters of QD-6.

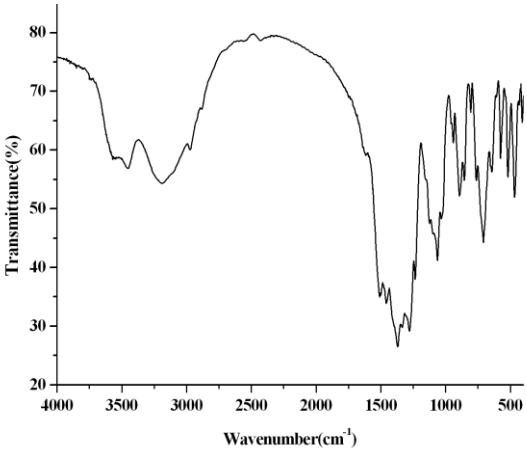

Figure S5. The IR spectra of QD-6.

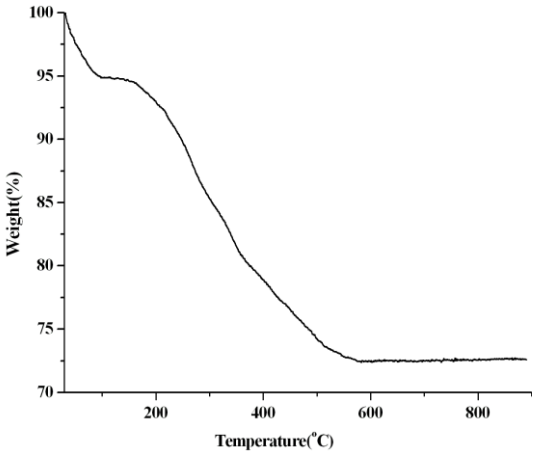

Figure S6. The TG curve of QD-6.

1. L. Y. Li, G. B. Li, M. Xiong, Y. X. Wang, J. H. Lin, *Acta Crystallogr., Sect. C* 2003, 59, i115.