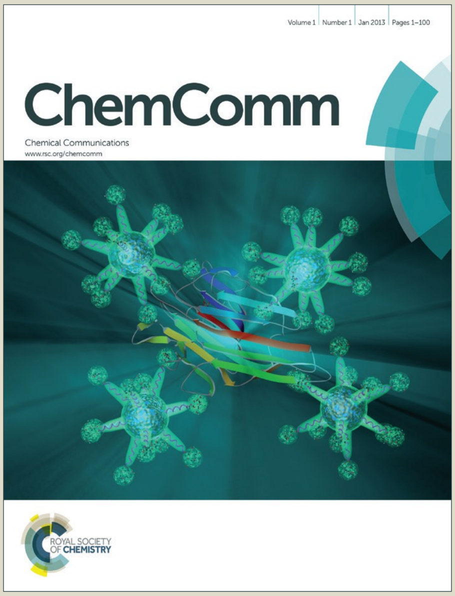

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

A zeolite CAN-type aluminoborate with gigantic 24-ring channels

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A cancrinite type aluminoborate with gigantic 24-ring channels has been made under solvothermal conditions using Al(*i*-PrO)$_3$ as Al source and amines as the structure directing agents. Its framework is alternately constructed from B_5O_{10} clusters and AlO_4 unit, no Al-O-Al linkages exist in the structure. Notably, the wall of the 24-ring channels has odd 11-ring windows, resulting in an unprecedented 3D intersecting channel system.

The rational design and synthesis of crystalline inorganic open frameworks with extra-large pores (more than 12-Ring, 12R) and low framework density are of great interest due to their rich structural chemistry and wide range of applications in catalysis, separation and ion exchange processes.[1,2] Up to now, several synthetic approaches have been developed to obtain large-pore materials by modifying the wall composition and connectivity, and further changing the pore size and shape.[3-7] For example, several metal phosphates with 24R channels have been synthesized by using different organic amine cations as templates.[3] Four mesoporous germanates with channels from 30R to 48R were also known by incorporating different cluster building units.[4] Recently, Wang systemati-cally investigated the bimetallic gallium zincophosphites using straight aliphatic monoamines as templates, and made a series of NTHU-13 with channel expansion from 24R to 72R.[6] It is believed that the combination of larger cluster building units in the framework can lead to the larger pores as predicted by Férey in terms of scale chemistry.[8]

Since the discovery of aluminosilicate zeolites, Al has been used in making numerous artificial zeolites. In 1973, Al was introduced into the borate system by Lehmann et al,[9] they obtained three aluminoborates (ABOs) with B:Al ratios of 3:1, 2:1, and 2:3. After that, several ABO phases were identified under hydrothermal conditions,[10] their structures remain unknown because it is difficult to obtain suitable crystals for structure determination. Recently, Lin and co-workers synthesized two ABOs with large pores of 18R and 24R (denoted as PKU-1/2) by using the boric acid flux method.[11] Due to the poor crystallization, the detailed structures of PKU-1/2 were established by analysis of the X-ray powder diffraction data combined with high-resolution TEM data. Notably, ABOs obtained under boric acid flux condition usually contain AlO_6 octahedra and edge-sharing Al-O-Al bonds,[11-12] these characteristics are different to the zeolite-type 4-connected porous frameworks composed of corner-sharing tetrahedra.

Borates show rich structural chemistry and easy to form different cluster building units.[13] In addition, polyborate anions are a remarkable source of nonlinear optical materials due to the asymmetric electronic distributions on the distorted planar borate rings, two notable examples are $[B_3O_6]^{3-}$ in β-BaB_2O_4 (BBO) and $[B_3O_7]^{5-}$ in LiB_3O_5 (LBO).[14,15] Therefore, it's interesting to use polar or asymmetric B–O cluster building units to replace tetrahedral SiO_4 in zeolite to form chiral zeolitic frameworks with large surface area and low-density.[7d,16] Since 2009, we have developed a synthetic approach to obtain organic amines and transition-metal complex templated zeolite-like ABOs under hydro(solvo)thermal conditions using Al(*i*-PrO)$_3$ as Al source.[17] These well crystalline open-framework ABOs show different types of four-connected net such as ABW, CrB_4 and diamond, and contain channels from 7R to 20R. In this study, we present a novel open-framework ABO, namely $[CH_3NH_3]_{1.5}[CH_3CH_2CH_2NH_3]_{0.5}[H_2O]_5[Al(B_5O_{10})]$ (denoted as BIT-1, Beijing Institute of Technology), which contain 24-ring channels (Fig. 1) by incorporating B_5O_{10} clusters. BIT-1 exhibits a zeolite CAN-type net with a very low density and high nonframework volume in inorganic open framework materials. The discovery of BIT-1 pushed the maximum ABO pore opening from 20R to 24R under hydro(solvo)thermal

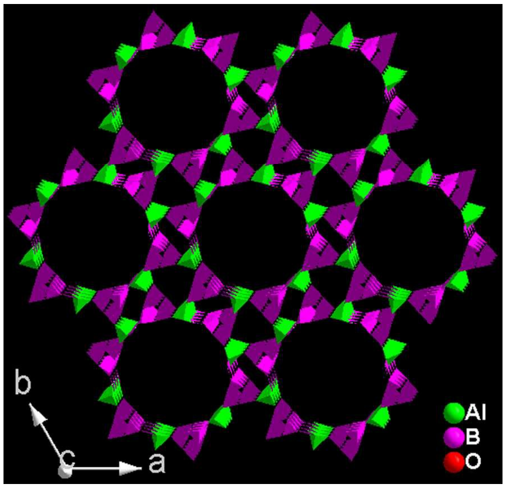

Fig 1. Framework structure of BIT-1 viewed along the [001] direction showing 24R, 9R and 8R channels, respectively.

conditions.

BIT-1 was made by the solvothermal reaction of H_3BO_3, Al(*i*-PrO)$_3$ (aluminium isopropoxide), methylamine alcohol solution (MAS, V(CH_3NH_2):V(CH_3CH_2OH) = 1:2) and *n*-propylamine in a 40 mL Teflon-lined stainless steel autoclave at 170ºC for 7 days (pH = 9). Pure colorless prismatic crystals were obtained in a yield of about 90% based on Al(*i*-PrO)$_3$. The phase purity of BIT-1 was confirmed by the agreement between the experimental and simulated powder X-ray diffraction patterns (Fig. S1). In the absence of *n*-propylamine, we have only obtained a previous reported ABO.[17d]

BIT-1 crystallizes in the hexgonal space group $P6_3$ (No. 173) (Table S1). The framework is made of strict alternation of B_5O_{10} clusters and AlO_4 tetrahedra. Each B_5O_{10} cluster consists of two B_3O_3 rings with one BO_4 tetrahedron and four BO_3 triangles, B_3O_3 rings are almost perpendicular to each other. Each B_5O_{10} cluster connects with ten neighboring others through four bridging AlO_4 tetrahedra, and each AlO_4 group linked to ten nearest neighbors by four bridging B_5O_{10} clusters. Such a connection of the B_5O_{10} clusters and AlO_4 gives rise to a 3D anionic framework with parallel 24R, 8R and 9R channels running along the [001] direction (Fig. 1). The Al–O and B–O bond lengths are in agreement with those observed in other ABOs (Table S2).[17] Each 24R channel is surrounded by six 8R and six 9R channels. The 24R channel is built from six AlO_4 and six BO_4 tetrahedra, as well as twelve BO_3 triangles containing six repeating $-BO_3-BO_4-BO_3-AlO_4-$ linkages with diameter of 16.77×16.74 Å (The distance between two O atoms, Fig. 2b, S2b), which is larger than other 24R channels and comparable to 40R channels in 40R-NTHU-13 (15.2×15.2 Å).[6] The diameters of 8R and 9R are about 7.47×4.84 Å and 7.24×5.97 Å (The distance between two O atoms), respectively (Fig. 2c,d,S2c,d). The wall of the 24R channels includes odd 11R windows (Fig. 2a) resulting in an 3D intersecting-channel framework. From the topological point of view, the framework of BIT-1 will be reduced into a rare zeolite CAN (cancrinite) type net, in which both B_5O_{10} clusters and AlO_4 tetrahedra act as 4-connected nodes (Fig. S3).

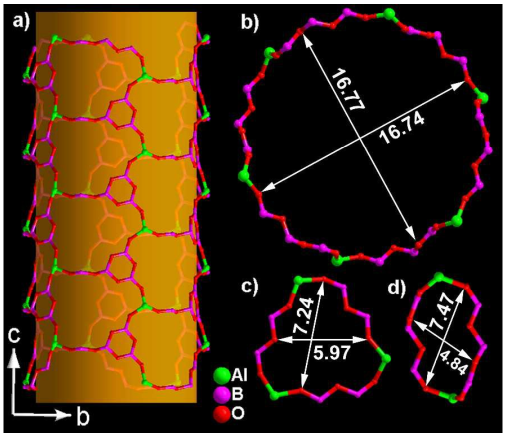

Fig 2. (a) Side view of one 24R channel along [100] direction showing 11R side pockets. (b,c,d) The pore size of 24R, 9R and 8R channels, respectively.

The protonated methylamine and water molecules are located within the smaller 8R and 9R channels, these species interact with the inorganic wall through extensive hydrogen bonds (Fig. S2a, Table S3). According to the C/H/N elemental and thermogravimetric analyses, 1.5 protonated methylamine, 0.5 protonated *n*-propylamine and 5 water molecules are expected per formula (Fig. S4). The organic amines are protonated as counter-ions. Attempts to exchange the ammoniums with Na^+ and K^+ ions were unsuccessful, the collapse of the framework in the ion-exchange process indicates the H-bonds between the ammoniums and inorganic framework play an important role in stabilizing the structures.

To the best of our knowledge, PKU-2's 24R channels represent the largest pores in ABOs,[11b] which formed by 24 AlO_6 octahedra via edge-sharing Al–O–Al bonds, B_2O_5 and B_3O_7 units are attached in the Al-O frameworks. Notably, BIT-1 is significantly different from PKU-2, which shows a zeolite type net. Its 24R channel is built of AlO_4 tetrahedra and B_5O_{10} clusters via corner-sharing $-BO_3-BO_4-BO_3-AlO_4-$ linkages, resulting in no Al–O–Al connection in BIT-1. BIT-1 possesses a very low framework density and very high non-framework volume (Table 1). The nonframework volume of BIT occupies 63.4% of the whole unit cell volume, which exceeds other reported 24R channel structures, and even larger than 40R-NTHU-13 (61.7%).[6] The distinct structural type between BIT-1 and PKU-2 may attributed to different synthetic methods. The well crystalline BIT-1 was made under solvothermal condition using amines as templates, while the poor crystalline PKU-2 was made in boric acid flux without

Table 1. Selected inorganic open frameworks with extra-large pore

Material	Ring size	Calculated density	Non-framework volume	Ref.
72R-NTHU-13	72	1.188	75.7%	[6]
64R-NTHU-13	64	1.297	72.3%	[6]
56R-NTHU-13	56	1.337	70.5%	[6]
48R-NTHU-13	48	1.521	66.2%	[6]
40R-NTHU-13	40	1.554	61.7%	[6]
28R-NTHU-13	28	1.779	51.7%	[6]
NTHU-5	26	1.811	52%	[7b]
NTHU-1	24	2.124	42%	[3c]
Cr-NKU-24	24	1.775	46%	[7c]
SCU-24	24	1.369	57.9%	[7e]
ND-1	24	2.125	50%	[3a]
VSB-5	24	2.580	36%	[3d]
SU-M	30	1.692	50.8%	[4a]
ITQ-37	30	1.980		[4b]
JLG-12	30	2.128	58%	[4c]
PKU-17	48	1.404	70.3%	[4d]
SU-61	26	1.738		[5e]
FDU-4	24	2.399		[5a]
FJ-1	24	2.839		[5b]
ASU-16	24	2.307		[5c]
BIT-1	24	1.434	63.4%	this work

any organic template.

The polar space group $P6_3$ of BIT-1 prompts us to evaluate its second-order nonlinear optical properties. Second harmonic generation (SHG) measurement was carried out on a sieved powder sample by the Kurtz-Perry method at room temperature.[18] SHG measurements on a Q-switched Nd:YAG laser (1064 nm) revealed that BIT-1 exhibits a moderate SHG response about 1.1 times that of KDP (KH_2PO_4) powder, and it is phase matchable (Fig. 3). Optical diffuse reflectance studies reveal that the BIT-1 is a wide-band-gap semiconductor with a band gap of 5.92 eV (Fig. S5). The band structure of solid-state BIT-1 shows a direct band gap of about 6.44 eV, which is comparable with the experiment value (Fig S6a, Table S4). The calculation excluded the effect of the guest molecules. The bands can be assigned according to total and partial density of states. The top valence bands (VBs) are mainly derived from O-2p and B-2p states; the bottom conduction bands (CBs) are mainly contributed from Al-3p and B-2p states (Fig. S6b).

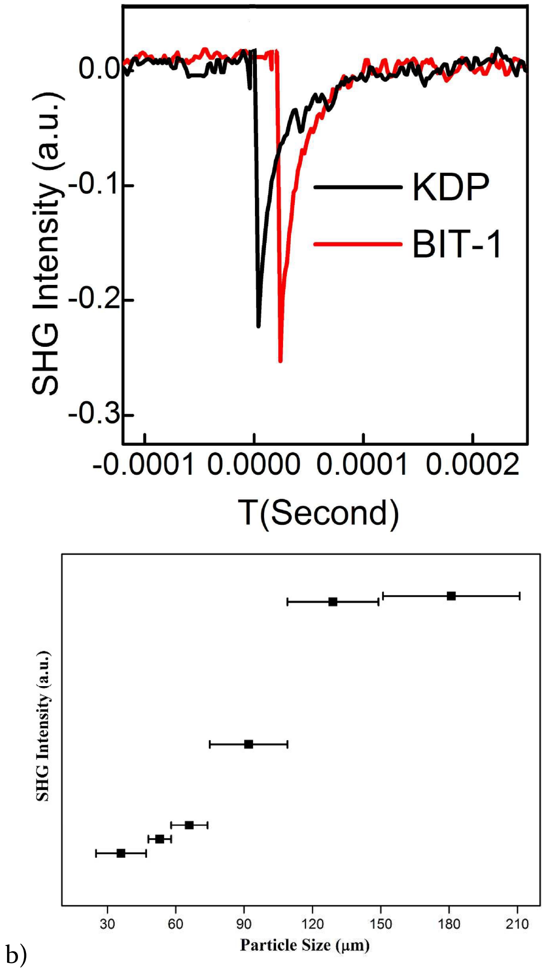

Fig 3. (a) Comparison of the measured SHG response of BIT-1 with that of KDP in the same particle size of 75–109 μm; (b) phase-matching curve for BIT-1.

In summary, a well crystalline chiral ABO with large 24R channels has been successfully obtained under solvothermal conditions. The framework can be described as a zeolite CAN-type net structure, and exhibits a very low framework density and high nonframework volume by incorporating B_5O_{10} clusters and AlO_4 tetrahedra. The successful isolation of BIT-1 demonstrates that using oxoboron clusters as building blocks is a feasible route to make inorganic open frameworks with extra-large pores. Further work is in progress.

This work was supported by the NSFC (no. 91122028, 21571016 and 21471130), the 973 program (no. 2014CB932-101), the NSFC for Distinguished Young Scholars (no. 20725-101), the NSF of Zhejiang Province (no. LY13B010002), and the Open Research Fund of Top Key Discipline of Chemistry in Zhejiang Provincial Colleges and Key Laboratory of the Ministry of Education for Advanced Catalysis Materials (Zhejiang Normal University).

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† Electronic Supplementary Information (ESI) available: Eeperimetal section and additional characterizing data. CCDC-953421. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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