Zeotype Frameworks

DOI: 10.1002/anie.201402663

A 3D Aluminoborate Open Framework Interpenetrated by 2D Zinc–Amine Coordination-Polymer Networks in Its 11-Ring Channels**

Li Wei, Qi Wei, Zhi-En Lin, Qin Meng, Huan He, Bai-Feng Yang, and Guo-Yu Yang**

Abstract: *A new inorganic–organic hybrid solid, [Zn(dap)$_2$]-[AlB$_5$O$_{10}$], combining the structural features of 3D open-framework inorganic solids and 2D metal–organic coordination polymers has been synthesized under solvothermal conditions. The compound displays extensive luminescence and moderate second-harmonic-generation efficiency.*

Crystalline open-framework inorganic solids are of current interest for their potential application in catalysis, separation, and ion exchange.[1] Aluminosilicate molecular sieves are the most well-known such materials with four-connected networks. Recently, great effort has been devoted to the synthesis of new zeotype materials by replacing SiO_4 tetrahedra with tetrahedral oxoboron clusters.[2] A number of open-framework aluminoborates have been prepared in the presence of amines, inorganic cations, and discrete metal complexes as the structure-directing agents.[3] Unlike four-connected aluminosilicates, open-framework aluminoborates often contain unique BO_3 triangles in their structures. Such planar building units are highly desired in the design and synthesis of new optical materials with second-harmonic-generation (SHG) response.[4] A notable example is β-BaB_2O_4 (BBO), which exhibits excellent second-order nonlinear optical (NLO) properties.[5] It is expected that open-framework aluminoborates may integrate zeolitic porosity with the extraordinary optical properties of borate materials.

Functional coordination polymers constructed from metal ions and organic ligands are another expanding area for the exploration of porous materials.[6] The designable nature of organic ligands and their rich coordination geometries indicate that a huge number of porous coordination networks can be accessed and tuned. By using nanometer-sized organic ligands as the bridging units between metal ions, the pore sizes of coordination polymers can be readily extended to the mesoporous region.[7] These porous materials feature low density and a large surface area, and are therefore potential candidates for gas-storage applications.

The combination of both the compositional and structural features of zeotype inorganic solids and coordination polymers has resulted in the formation of a new class of porous materials known as inorganic–organic hybrid solids.[8] The frameworks of these materials consist of metal centers, inorganic anions, and organic ligands. The linkages between metal centers and inorganic anions usually produce low-dimensional substructures (e.g., discrete clusters, chains, and layers), which are further bridged by organic ligands to form inorganic–organic hybrid frameworks.[9] An illustrative example is NTHU-2 with zincophosphate layers pillared by 1,4-benzenedicarboxylate ligands.[10] In some cases, organic ligands attach to the inorganic backbones to fulfill the coordination environments of metal centers. They act as terminal ligands and do not affect the dimensionality of the hybrid structures. A common structural feature of these hybrid compounds is the presence of organic-ligand–metal–inorganic-anion linkages. Herein, we report a new type of inorganic–organic hybrid solid, namely, [Zn(dap)$_2$][AlB$_5$O$_{10}$] (**1**; dap = 1,3-diaminopropane), which contains two independent frameworks of different types: a two-dimensional (2D) zinc(II) coordination polymer and a 3D open-framework aluminoborate. No organic-ligand–metal–inorganic-anion linkages were observed in the hybrid structure. The coordination network is located in the pores of the open-framework aluminoborate. As far as we know, no such structural feature has been observed previously in open-framework compounds.

Colorless block crystals of compound **1** were obtained by the solvothermal reaction of a mixture of Al(*i*PrO)$_3$ (aluminium isopropoxide), $Zn(Ac)_2{\cdot}2H_2O$, H_3BO_3, dap, H_2O, and pyridine at 180 °C for 7 days in a Teflon-lined stainless-steel autoclave. The powder X-ray diffraction pattern of the as-synthesized compound was in good agreement with that simulated on the basis of single-crystal data, thus indicating the phase purity of the as-synthesized compound (Figure 1). The IR spectrum indicated the existence of both trigonally and tetrahedrally coordinated boron atoms (see Figure S1 in the Supporting Information). The bands at 1354 and 1216 cm^{-1} are characteristic of the asymmetric stretch of BO_3 units, whereas the bands for BO_4 units appear at 1043 and 928 cm^{-1}.

Single-crystal structural analysis revealed that compound **1** crystallizes in the orthorhombic space group $Pna2_1$. The asymmetric unit contains one unique Zn atom, one Al atom,

---

[*] L. Wei, Q. Meng, H. He, B.-F. Yang, Prof. Dr. G.-Y. Yang
MOE Key Laboratory of Cluster Science
School of Chemistry, Beijing Institute of Technology
Beijing 100081 (China)
E-mail: ygy@bit.edu.cn
Dr. Z.-E. Lin
College of Chemistry, Sichuan University
Chengdu, Sichuan 610064 (China)
E-mail: zhienlin@scu.edu.cn
Q. Wei, Prof. Dr. G.-Y. Yang
State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences
Fuzhou, Fujian 350002 (China)
E-mail: ygy@fjirsm.ac.cn

[**] This research was supported by the NSFC (nos. 91122028, 21221001, and 20725101) and the 973 Program (nos. 2014CB932101 and 2011CB932504).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201402663.

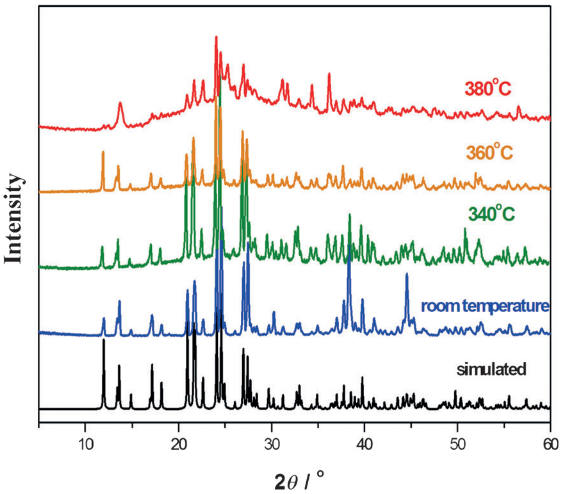

Figure 1. Simulated and experimental powder XRD patterns of **1** upon treatment at different temperatures.

one B_5O_{10} cluster, and two dap molecules (Figure 2a). Each Zn atom is coordinated by four N atoms from different dap molecules to form a tetrahedral coordination geometry. The dap molecules act as bridging ligands between two Zn atoms. The Al atom is tetrahedrally coordinated by four O atoms from adjacent B_5O_{10} clusters. Two coordination models for B atoms were observed in the oxoboron cluster: BO_3 triangles and a BO_4 tetrahedron. The BO_4 tetrahedron is located at the center of the B_5O_{10} cluster and shares its four O corners with four BO_3 triangles. The average Zn–N, Al–O, and B–O bond lengths are 2.034, 1.745, and 1.396 Å, respectively, in good agreement with those observed in other open-framework metal borates.

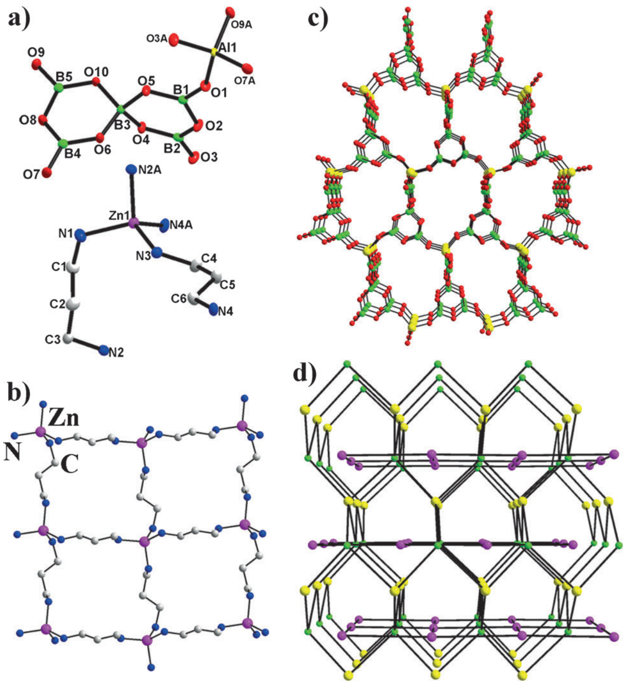

Figure 2. a) Asymmetric unit of **1**. b) 2D network of the zinc(II) coordination polymer in the *ab* plane. c) View of the 3D open framework of the aluminoborate along the *b* axis. d) Topological view of the structure of **1**: The zinc(II) coordination network is located in the pores of the open framework of the aluminoborate. Zn purple, Al yellow, B/B_5O_{10} green, O red, C gray, N blue.

The most striking structural feature of compound **1** is the presence of two independent frameworks of different types: a metal–organic coordination network and an inorganic aluminoborate framework. The coordination network is built up from strictly alternating Zn atoms and dap molecules. Each Zn atom is connected to four dap molecules, and each dap molecule is connected to two zinc atoms. Such connection generates infinite layers parallel to the *ab* plane (Figure 2b). These layers have an sql topology with a shortest Zn···Zn distance of 7.233 Å. They are stacked along the [001] direction in an ABAB sequence. The inorganic aluminoborate framework is generated by strictly alternating B_5O_{10} clusters and AlO_4 tetrahedra (Figure 2c). By regarding these building units as four-connected nodes, the inorganic framework could be understood as a four-connected network with a diamond topology. The sql-type coordination network and the diamond-type inorganic network interpenetrate with one another to form a new type of inorganic–organic hybrid framework (Figure 2d). The two different networks interact with each other through extensive hydrogen bonding. The shortest N···O distances are in the region of 2.943(3)–3.215(4) Å.

There are 11-ring channels along the [100] and [010] directions in the inorganic aluminoborate framework (see Figure S2). The pore size, defined by three AlO_4 tetrahedra, six BO_3 triangles, and two BO_4 tetrahedra, has a free pore diameter of 10.52 × 6.98 Å (1.35 Å was assumed as the van der Waals radius of an oxygen atom). Channels defined by rings containing an even number of non-oxygen atoms (e.g. 8-, 10-, and 12-membered rings) are often found in zeotype inorganic solids. In comparison, "odd-ring" channels are rarely observed. The presence of B_5O_{10} clusters may favor the formation of such channels. Viewed along the [001] direction, it seems that the framework has 8-ring channels. Careful analysis of the structure reveals that the "8-ring" window is unclosed. The actual channels running along the [001] direction are helical with a pitch of 14.799(6) Å (Figure 3). Both left-handed and right-handed helices exist in the structure, and are further coupled with each other to form the 3D inorganic framework. Void-space analysis with the program PLATON indicated that the inorganic framework occupies 42.8 % of the unit-cell volume, thus leaving 57.2 % (904.6 $Å^3$ out of the unit-cell volume of 1580.7 $Å^3$) as "solvent-accessible" space.[11]

It is believed that the coordination network of the zinc(II) coordination polymer may play a structure-directing role in the formation of the 3D aluminoborate framework. Previously, three types of templating agents have been adopted to direct the formation of open-framework aluminoborates and other related zeotype materials: inorganic cations, organic cations, and metal complexes. All the metal complexes exist in the isolated-ion form, containing metal centers and organic ligands. The presence of a zinc(II) coordination polymer in the pores of the open-framework aluminoborate is unprecedented.

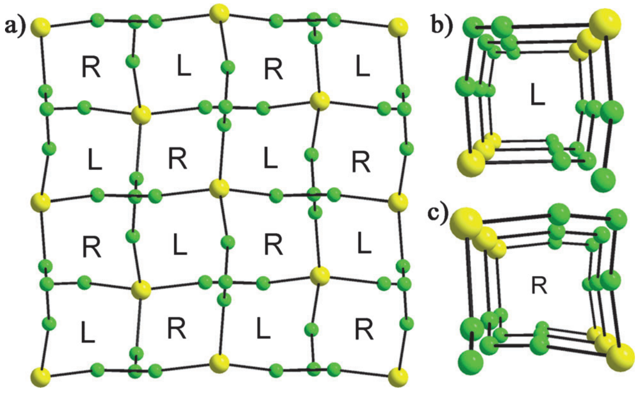

Figure 3. a) Topological view of the structure of **1** along the [001] direction, showing the left-/right-handed helical channels (b,c). Al, yellow, B/B_5O_{10} green.

Thermogravimetric analysis, performed under a flow of air with a heating rate of 10 °C min^{-1}, showed that compound **1** remains stable up to about 370 °C (see Figure S3). On further heating, a gradual weight loss of 32.5 % up to 1000 °C was observed and assigned to the removal of the dap molecules (calcd: 31.96 %). Powder XRD analysis indicated that the structure of **1** remains stable until at least 360 °C (Figure 1). When the polycrystalline sample was heated at 380 °C, its framework started to collapse.

Compound **1** displays a broad emission band with a peak maximum at 420 nm as a result of excitation at 327 nm (Figure 4). Since compound **1** crystallizes in the acentric space group $Pna2_1$, we examined its second-order nonlinear optical properties. Measurement of the powder frequency-doubling effect was carried out on a sieved powder sample of the compound by means of the Kurtz–Perry method.[12] The fundamental wavelength was 1064 nm and was generated by a Q-switched Nd:YAG laser. The SHG wavelength was 532 nm. KH_2PO_4 (KDP) powder was used as a reference. The SHG measurements, conducted on a Q-switched Nd:YAG laser with the sieved powder samples (70–100 mesh), revealed that **1** displays an SHG efficiency that is about 1/3 that of KDP (see Figure S4). The result confirms the absence of a center of symmetry in compound **1**. The UV/Vis/NIR diffuse reflectance spectrum of the polycrystalline sample of compound **1** showed that **1** has an adsorption onset at 213 nm, thus indicating that **1** is a wide-gap semiconductor with a bad gap of 5.82 eV (see Figure S5). The adsorption band in the region of 210–295 nm is caused by the presence of a zinc–amine coordination network in the channels of the aluminoborate.

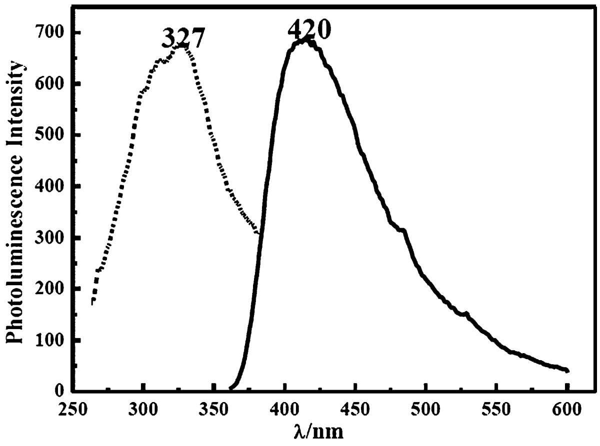

Figure 4. Excitation and emission spectra of **1** at room temperature.

In summary, a new inorganic–organic hybrid solid has been successfully made under solvothermal conditions. This compound displays extensive luminescence and exhibits moderate SHG efficiency. It bridges the gap between two different types of solid-state materials: coordination polymers and zeolitic inorganic solids. The zinc(II) coordination network is ordered within the pores of the aluminoborate framework, thus demonstrating a possible supramolecular templating approach to open-framework inorganic solids. Since the topologies of coordination networks can be readily tuned by the judicious choice of organic ligands and metal centers, we believe that this synthetic approach will offer exciting opportunities to create new crystalline hybrid materials with diverse structures and interesting properties.

Experimental Section

Synthesis of **1**: A mixture of $Al(iPrO)_3$ (0.204 g), $Zn(Ac)_2{\cdot}2H_2O$ (0.220 g), and H_3BO_3 (0.360 g) was dispersed in a mixed solvent composed of pyridine (3.2 mL) and water (2 mL) and stirred for about 2 h. 1,3-Diaminopropane (1.5 mL) was then slowly added with constant stirring. The final mixture (pH 9) was sealed in a 25 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 7 days under autogenous pressure, then cooled to room temperature. Colorless block crystals of **1** (80 % yield based on Al) were obtained by filtration, washed with distilled water, and dried in air. Elemental analysis: calcd (%) for $C_6H_{20}ZnAlB_5N_4O_{10}$ (**1**): C 15.85, H 4.43, N 12.32; found: C 15.46, H 4.30, N 11.39; IR (KBr): $\tilde{\nu}$ =3416 (w), 3237 (w), 3154 (w), 2962 (w), 1617 (s), 1354 (m), 1216 (m), 1043 (m), 1005 (m), 928 (m), 861 (m), 780 (w), 720 (m), 675 (m), 467 cm^{-1} (w).

Crystal data of **1**: $M_r = 454.66$, orthorhombic, $Pna2_1$, $a = 14.7659(3)$, $b = 7.2332(2)$, $c = 14.7996(3)$ Å, $V = 1580.67(5)$ Å^3, $Z = 4$, $\rho = 1.911$ g cm^{-3}, $\mu = 1.672$ mm^{-1}, $F(000) = 928$, GOF = 1.081; a total of 4643 reflections were collected in the range of $3.13° \leq \theta \leq 25.00°$, 2095 of which were unique ($R_{int} = 0.0195$); $R_1(wR_2) = 0.0200$ (0.0508) for 244 parameters and 2055 reflections ($I > 2\sigma(I)$). CCDC 930546 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.

Received: February 24, 2014

Keywords: aluminoborates · coordination polymers · open frameworks · organic–inorganic hybrid composites · supramolecular templates

[1] a) J. Jiang, J. Yu, A. Corma, *Angew. Chem.* **2010**, *122*, 3186; *Angew. Chem. Int. Ed.* **2010**, *49*, 3120; b) J. Yu, Xu, *Acc. Chem. Res.* **2010**, *43*, 1195.
[2] Z.-E. Lin, G.-Y. Yang, *Eur. J. Inorg. Chem.* **2011**, 3857.
[3] a) C. Rong, Z. Yu, Q. Wang, S.-T. Zheng, C.-Y. Pan, F. Deng, G.-Y. Yang, *Inorg. Chem.* **2009**, *48*, 3650; b) J. Zhou, S.-T. Zheng, M.

Zhang, G.-Z. Liu, G.-Y. Yang, *CrystEngComm* **2009**, *11*, 2597; c) J. Zhou, W.-H. Fang, C. Rong, G.-Y. Yang, *Chem. Eur. J.* **2010**, *16*, 4852; d) A. K. Paul, S. Natarajan, *Cryst. Growth Des.* **2010**, *10*, 765; e) G.-J. Cao, J. Lin, J.-Y. Wang, S.-T. Zheng, W.-H. Fang, G.-Y. Yang, *Dalton Trans.* **2010**, *39*, 8631; f) G.-J. Cao, J. Lin, W.-H. Fang, S.-T. Zheng, G.-Y. Yang, *Dalton Trans.* **2011**, *40*, 2940; g) G.-Z. Liu, L.-Y. Xin, L.-Y. Wang, *Inorg. Chem. Commun.* **2011**, *14*, 775.

[4] a) S. Wang, N. Ye, *J. Am. Chem. Soc.* **2011**, *133*, 11458; b) F. Kong, H.-L. Jiang, T. Hu, J.-G. Mao, *Inorg. Chem.* **2008**, *47*, 10611; c) Z.-T. Yu, Z. Shi, Y.-S. Jiang, H.-M. Yuan, J.-S. Chen, *Chem. Mater.* **2002**, *14*, 1314.

[5] C. Chen, B. Wu, A. Jiang, G. You, *Sci. Sin. Ser. B (Engl. Ed.)* **1985**, *28*, 235.

[6] a) J.-P. Zhang, Y.-B. Zhang, J.-B. Lin, X.-M. Chen, *Chem. Rev.* **2012**, *112*, 1001; b) R. E. Morris, X. Bu, *Nat. Chem.* **2010**, *2*, 353; c) A. Corma, H. García, F. X. Llabrés i Xamena, *Chem. Rev.* **2010**, *110*, 4606; d) S. Kitagawa, R. Kitaura, S.-i. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334.

[7] a) H. Deng, C. J. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang, O. M. Yaghi, *Science* **2010**, *327*, 846; b) D. Zhao, D. J. Timmons, D. Yuan, H.-C. Zhou, *Acc. Chem. Res.* **2011**, *44*, 123; c) W. Xuan, C. Zhu, Y. Liu, Y. Cui, *Chem. Soc. Rev.* **2012**, *41*, 1677.

[8] a) K. Sumida, M. R. Hill, S. Horike, A. Dailly, J. R. Long, *J. Am. Chem. Soc.* **2009**, *131*, 15120; b) M. Kang, D. Luo, Z. Lin, G. Thiethe, S. Dehnen, *CrystEngComm* **2013**, *15*, 1845; c) S.-H. Huang, C.-H. Lin, W.-C. Wu, S.-L. Wang, *Angew. Chem.* **2009**, *121*, 6240; *Angew. Chem. Int. Ed.* **2009**, *48*, 6124; d) F. Wang, Z.-S. Liu, H. Yang, Y.-X. Tan, J. Zhang, *Angew. Chem.* **2011**, *123*, 470; *Angew. Chem. Int. Ed.* **2011**, *50*, 450.

[9] a) A. K. Cheetham, C. N. R. Rao, R. K. Feller, *Chem. Commun.* **2006**, 4780; b) D. Maspoch, D. Ruiz-Molina, J. Veciana, *Chem. Soc. Rev.* **2007**, *36*, 770.

[10] Y.-C. Liao, F.-L. Liao, W.-K. Chang, S.-L. Wang, *J. Am. Chem. Soc.* **2004**, *126*, 1320.

[11] A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.

[12] S. K. Kurtz, T. T. Perry, *J. Appl. Phys.* **1968**, *39*, 3798.