DOI: 10.1002/anie.200604946

White Phosphors

A White-Light-Emitting Borate-Based Inorganic–Organic Hybrid Open Framework**

Ming-Sheng Wang, Guo-Cong Guo, Wen-Tong Chen, Gang Xu, Wei-Wei Zhou, Ke-Jun Wu, and Jin-Shun Huang*

Open-framework inorganic materials, which find use in catalysis, separation, and ion exchange, have undergone enormous growth in the last decades.[1] Hitherto, inorganic borates with remarkable open frameworks, such as pringleite, ruitenbergite, and penobsquisite, were rarely reported.[2] Although organically modified open-framework borosilicates and borophosphates have received a certain amount of attention, many other borate systems need further exploration. Like the isopolyacid system, most of the reported organically modified borates show molecular structures, and those with extended structures are extremely rare.[3] Further studies on inorganic–organic hybrid open-framework borates are of fundamental importance.

Other important applications of borates are based on their optical properties, for example, nonlinear optics[4] and photoluminescence (PL).[5] There is growing interest in developing white-light-emitting devices for applications in displays and lighting. The main approaches adopted currently to produce white light include employment of a UV LED to excite red, green, and blue (RGB) phosphors, a blue LED to excite a yellow phosphor, or three LEDs to generate RGB lights individually, in accordance with the tricolor theory.[6] White-light-emitting devices with multiple emitting components, which are generally rather complicated and expensive, can be problematic as color balance is difficult to control.[7] Most of these problems can be avoided by using single-emitting-component (SEC) phosphors. Thus far, research on SEC intrinsic white-light-emitting phosphors has mainly focused on polymers, such as Si-based materials[8] and polyfluorene derivatives,[9] and inorganic materials doped with rare earth metal ions.[10] In contrast, the field of SEC white-light-emitting borate phosphors remains vacant.

Herein we present two three-dimensional (3D) inorganic–organic hybrid isopolyacid borates, namely, B_6O_9(en) (**1**) and $(H_2en)_2(Hen)_2B_{16}O_{27}$ (**2a**; en = ethylenediamine).[11] They respectively form interpenetrating and noninterpenetrating open frameworks. White-light-emitting inorganic–organic hybrid open frameworks were rarely reported.[12] Notably, the photoluminescence of **2a** can be modified from blue to white by means of a simple heat-treatment process.

Compound **1** was obtained by solvothermal reaction of H_3BO_3 and en at 180 °C. The synthesis of **2a** was as for **1**, except that DMF or acetone was added. Powder X-ray diffraction (PXRD) studies indicate that the products are phase-pure, because the experimental diffraction peaks correspond well with those simulated on the basis of single-crystal structures (see Figures S1 and S2).

The crystal structure of **1** is composed of a twofold interpenetrating 3D en-pillared borate-based open framework (Figure 1 a and d) with 12-ring (12R) channels along the c direction (Figure 1 b). The independent unit contains one en molecule and six boron polyhedra, of which four are triangular and two tetrahedral (Figure S3). The B−O bonds around the tetrahedral B atoms are about 0.085 Å longer than those surrounding the trigonal B atoms.

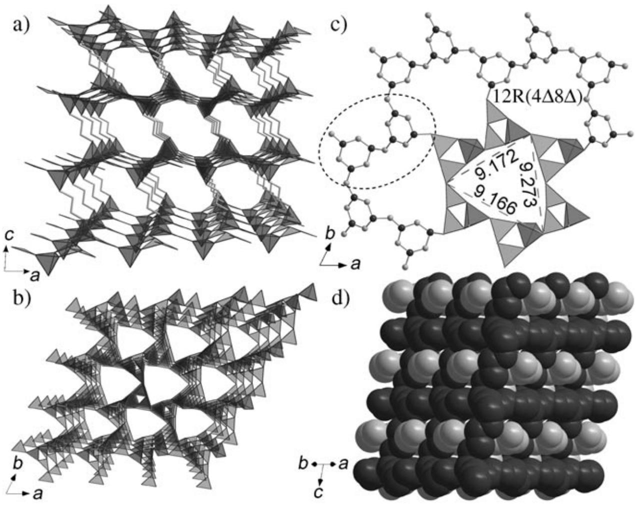

Figure 1. 3D open frameworks of **1** along the *b* (a) and *c* (b) directions, 2D layer of 3,12-membered rings with the dashed circle showing the FBB (c), and the twofold interpenetrating crystal structure (d).

A striking characteristic of **1** is the presence of neutral 2D $[B_6O_9]$ layers (Figure 1 c).[2] Benzene-like 3-ring and triangular 12-ring units coexist in the layer. The lengths of the three edges of the triangular ring are 9.172(2), 9.273(2), and 9.166(2) Å. The fundamental building block (FBB) of the layer comprising two BO_4 tetrahedra (□) and four BO_3

---

[*] Dr. M.-S. Wang, Prof. Dr. G.-C. Guo, W.-T. Chen, G. Xu, W.-W. Zhou, K.-J. Wu, Prof. J.-S. Huang
State Key Lab of Structural Chemistry
Fujian Institute of Research on the Structure of Matter
Chinese Academy of Sciences
Fuzhou, Fujian 350002 (P.R. China)
Fax: (+86) 591-8371-4946
E-mail: gcguo@ms.fjirsm.ac.cn

[**] We gratefully acknowledge financial support by the NSF of China (20571075, 20521101), the NSF for Distinguished Young Scientist of China (20425104), Key Project from CAS and the NSF of Fujian Province (2006J0013).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

triangles (△) can be described as 2□4△:⟨2△□⟩⟨2△□⟩.[2] Thus far, nine kinds of FBBs have been discovered in 2D borate compounds.[2] The FBB in **1** is a new type, to the best of our knowledge.

Compound **2a** forms a 3D anionic noninterpenetrating open framework and is the first 3D ammonium borate (Figure 2a). The crystallographically independent unit includes five trigonal and three tetrahedral B atoms (Figure S4). The B−O bond lengths are analogous to those in **1**. The framework has 13R and 14R channels along the *c* direction, of which the minimum circuits individually have descriptors of 6□7△:⟨□□△□△△△□△□△□△⟩ and 6□8△:⟨□△△□△□△□△□△□△△⟩ (Figure 2b). The protonated en molecules in **2a** act as guests to balance the charge. The void space of the framework corresponds to 46.1 % of the unit-cell volume, which is close to that of zeolite A.[13]

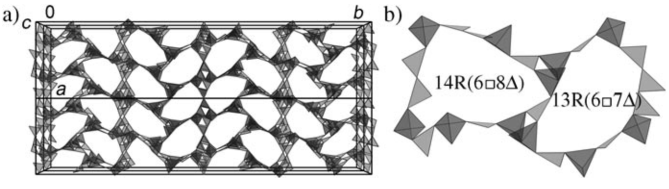

Figure 2. 3D open framework viewed along the *c* direction (a) and rings (b) for **2a**.

Organic amine molecules in as-synthesized borate-based frameworks mainly act as a kind of template, either protonated or coordinated to a metal center to form an isolated complex, but rarely participate in the framework.[3b,14] The en-pillared 3D open framework in **1** represents the first example of a layer structure with organic amine molecules as pillars in borate-based materials. The only known en-templated borate $(H_2en)B_4O_5(OH)_4$, which has a molecular structure, was obtained at room temperature.[15] Temperature may play a key role in the polymerization and dehydration of H_3BO_3 (see Scheme S1). While most ammonium-templated borate-based materials have hydroxy groups in their frameworks, both **1** and **2a** contain no hydroxy groups.

Heat treatment of colorless **2a** yields yellow **2b** at 250 °C and gray-yellow **2c** at 360 °C (Figure 3a). Yellow **2b** has a similar PXRD pattern to **2a**, that is, the framework is stable at 250 °C (Figures S2 and S5). However, the framework has collapsed in the gray-yellow **2c**, since its PXRD pattern differs from that of **2a**. Interestingly, solid samples **2a**–**c** display blue, white, and pale white photoluminescence, respectively, when illuminated with near-UV light (Figure 3a). Air-stable **2b** displays a broad visible PL spectrum that appears white to the eye. It has an external PL quantum yield of about 14.3 %,[16] which is close to that of the best sample reported by Hayakawa et al.[8c] The PL intensity of **2b** is higher than those of **2a** and **2c** (Figure 3b). The 460-nm band has a τ_f value of 5.79 ns, suggestive of its fluorescence character. The heat-treatment time influences the shape of the **2b** band. With increasing heat-treatment time, the full width at half-maximum (FWHM) increases and tends to saturation (Figure 3b, inset). This interesting phenomenon has not been found before. To improve the emission in the red-light range, we introduced Eu^{3+} ions into a sample of **2b** by soaking it in an aqueous solution of $EuCl_3$.[17] Whereas the resulting white-light-emitting sample **2b**-Eu has a weaker broad emission compared with **2b**, the emission peaks of Eu^{3+} ions reinforce the red-light emission (Figure 3).

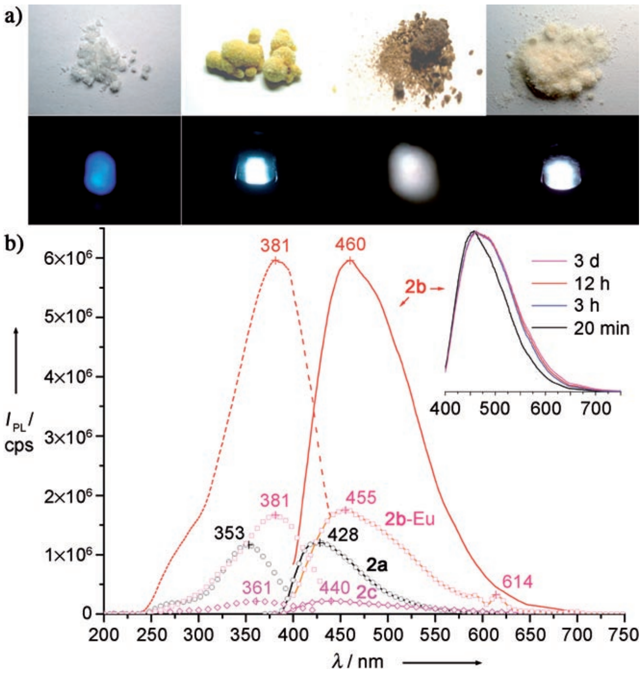

Figure 3. a) Images of the solid samples of **2a**–**c** and **2b**-Eu (top left to right) and their corresponding photoluminescence (λ_{ex}: 353 nm for **2a**, 381 nm for **2b**, 361 nm for **2c**,and 381 nm for **2b**-Eu) at room temperature. b) Solid-state PL spectra of **2a**–**c** and **2b**-Eu at room temperature. Inset: dependence of FWHM on heat-treatment time for **2b**.

The emission spectrum of **2b** has a 32-nm red shift compared with that of **2a**. A similar red shift was also found in B_2O_3 (Figure S7). Diffuse reflectance measurements show that **2a** and **2b** have band gaps of 2.99 and 1.92 eV, respectively (Figure S8). The narrower band gap of **2b** means increased transition probability of longer-wavelength photons, which is consistent with the red shift between **2a** and **2b**. Similarly, the band gap of B_2O_3 also becomes narrower when it is heated at 250 °C (Figure S9). Thus, the PL of **2a**,**b** should originate from the borate framework rather than the isolated ammonium ions. Since no metal activator ions exist in the sample, the self-activating PL of **2b** probably originates from structural defects caused by heat treatment.

In summary, we have prepared the first borate-based framework with organic amine molecules as pillars (**1**) and the first 3D ammonium borate (**2a**) under solvothermal conditions. These intriguing structures enrich the borate family. Especially zeolite-like **2a** with large void space may find utility in ion exchange in future. Compound **2b** is the first intrinsic white SEC phosphor in the borate system. Facile synthesis, moderate thermal stability, high PL intensity, cheap reactants, recyclable solvent, easy separation, zero metal content, and white-light emission make **2b** a good candidate for display and lighting applications.

Experimental Section

1: Typically, a mixture of H_3BO_3 (1.237 g, 20 mmol) and en (8 mL) was loaded into a 25-mL teflon-lined stainless steel autoclave, heated to 180 °C at a rate of 1 K min^{-1}, and then kept at 180 °C for 1 day, after which it was cooled to room temperature at a rate of 0.1 K min^{-1}. Colorless block crystals of **1** (341 mg, 38 % yield based on H_3BO_3) were obtained by filtering the final solution and successively washing the solid products with distilled water and acetone. C,H,N analysis (%) calcd for $C_2H_8B_6N_2O_9$: C 9.42, H 3.20, N 10.87; Found: C 8.86, H 3.01, N 10.39. The IR spectrum of **1** is shown in Figure S6a.

2a: The synthesis of **2a** was as for **1** except that DMF or acetone (0.5 mL) was added. Colorless prismatic crystals of **2a** (460 mg, 43 % yield based on H_3BO_3) were obtained by filtering the final solution and successively washing the solid products with distilled water and acetone. C,H,N analysis (%) calcd for $C_8H_{38}B_{16}N_8O_{27}$: C 11.29, H 4.50, N 13.16. Found: C 11.96, H 4.65, N 13.36. The IR spectrum of **2a** is shown in Figure S6b.

Heat treatment of **2a**: A colorless solid sample of **2a** was placed in an Al_2O_3 crucible, which was heated to 250 °C in a programmable furnace at a rate of 5 K min^{-1}, followed by a 3-h isothermal hold, after which it was cooled to room temperature to yield yellow **2b**. Gray-yellow **2c** was obtained as for **2b** except that the temperature was changed to 360 °C.

2b-Eu and its heat treatment: A yellow solid sample of **2b** was soaked in a 0.01 M aqueous solution of $EuCl_3$ for 2 h. The final mixture was filtered and the residue washed with distilled water, ethanol, and diethyl ether successively to yield a colorless solid, which was further heat-treated as for **2a** to give pale yellow **2b**-Eu. PXRD studies show that the framework of **2b** is retained in **2b**-Eu (Figure S2).

Received: December 7, 2006
Published online: April 19, 2007

Keywords: borates · boron · luminescence · solvothermal synthesis

---

[1] A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466; *Angew. Chem. Int. Ed.* **1999**, *38*, 3268.

[2] a) J. D. Grice, P. C. Burns, F. C. Hawthorne, *Can. Mineral.* **1999**, *37*, 731; b) P. C. Burns, J. D. Grice, F. C. Hawthorne, *Can. Mineral.* **1995**, *33*, 1131; c) M. Touboul, N. Penin, G. Nowogrocki, *Solid State Sci.* **2003**, *5*, 1327.

[3] a) G.-M. Wang, Y.-Q. Sun, G.-Y. Yang, *J. Solid State Chem.* **2004**, *177*, 4648; b) G.-Z. Liu, S.-T. Zheng, G.-Y. Yang, *Inorg. Chem. Commun.* **2007**, *10*, 84.

[4] a) P. Becker, *Adv. Mater.* **1998**, *10*, 979; b) T. Sasaki, Y. Mori, M. Yoshimura, Y. K. Yap, T. Kamimura, *Mater. Sci. Eng.* **2000**, *30*, 1; c) F. Kong, S.-P. Huang, Z.-M. Sun, J.-G. Mao, W.-D. Cheng, *J. Am. Chem. Soc.* **2006**, *128*, 7750; d) C. T. Chen, Y. B. Wang, B. C. Wu, K. C. Wu, W. L. Zeng, L. H. Yu, *Nature* **1995**, *373*, 322.

[5] a) T. Jüstel, H. Nikol, C. Ronda, *Angew. Chem.* **1998**, *110*, 3250; *Angew. Chem. Int. Ed.* **1998**, *37*, 3084; b) W.-G. Shu, L.-Z. Zheng, Z.-C. Zhou, *Chin. Rare Earths* **2002**, *23*, 77.

[6] a) W. A. Thornton, *J. Opt. Soc. Am.* **1971**, *61*, 1155; b) M. Koedam, J. Opstelten, *J. Light. Res. Technol.* **1971**, *3*, 205; c) J. M. P. J. Verstegen, D. Radielovic, L. E. Vrenken, *J. Electrochem. Soc.* **1974**, *121*, 1627.

[7] a) J. Kido, K. Hongawa, K. Okugama, K. Nagai, *Appl. Phys. Lett.* **1994**, *64*, 815; b) J. Kido, H. Shionoya, K. Nagai, *Appl. Phys. Lett.* **1995**, *67*, 2281; c) J. P. Yang, Y. D. Jin, P. L. Heremans, R. Hoefnagels, P. Dieltiens, F. Blockhugs, H. J. Geise, M. van der Auweraer, G. Borghs, *Chem. Phys. Lett.* **2000**, *325*, 251.

[8] a) W. H. Green, K. P. Le, J. Grey, T. T. Au, M. J. Sailor, *Science* **1997**, *276*, 1826; b) T. Uchino, T. Yamada, *Appl. Phys. Lett.* **2004**, *85*, 1164; c) T. Hayakawa, A. Hiramitsu, M. Nogami, *Appl. Phys. Lett.* **2003**, *82*, 2975; d) K. L. Paik, N. S. Baek, H. K. Kim, J.-H. Lee, Y. Lee, *Macromolecules* **2002**, *35*, 6782; e) L. D. Carlos, R. A. Sá Ferreira, R. N. Pereira, M. Assuncüão, V. de Zea Bermudez, *J. Phys. Chem. B* **2004**, *108*, 14924.

[9] a) S. K. Lee, D.-H. Hwang, B.-J. Jung, N. S. Cho, J. Lee, J.-D. Lee, H.-K. Shim, *Adv. Funct. Mater.* **2005**, *15*, 1647; b) G. Tu, Q. Zhou, Y. Cheng, L. Wang, D. Ma, X. Jing, F. Wang, *Appl. Phys. Lett.* **2004**, *85*, 2172; c) G. Tu, C. Mei, Q. Zhou, Y. Cheng, Y. Geng, L. Wang, D. Ma, X. Jing, F. Wang, *Adv. Funct. Mater.* **2006**, *16*, 101.

[10] a) B. Liu, C. Shi, Z. Qi, *Appl. Phys. Lett.* **2005**, *86*, 191111; b) Y. Q. Li, G. de With, H. T. Hintzen, *J. Mater. Chem.* **2005**, *15*, 4492; c) S. Sivakumar, F. C. J. M. van Veggel, M. Raudsepp, *J. Am. Chem. Soc.* **2005**, *127*, 12464; d) Y. Mita, T. Kobayashi, Y. Miyamoto, O. Ishii, N. Sawanobori, *Phys. Status Solidi B* **2004**, *241*, 2672; e) W. Yang, T.-M. Chen, *Appl. Phys. Lett.* **2006**, *88*, 101903; f) L. D. Carlos, R. A. Sá Ferreira, V. De Zea Bermudez, *Phys. Rev. B* **1999**, *60*, 10042.

[11] Crystal data for **1**: $C_2H_8B_6N_2O_9$, $M_r = 268.96$, triclinic, $P\bar{1}$, $a = 8.5974(2)$, $b = 8.6545(7)$, $c = 8.6814(7)$ Å, $\alpha = 64.36(1)$, $\beta = 75.13(1)$, $\gamma = 60.55(1)°$, $V = 506.32(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.764$ Mg m^{-3}, $\mu = 0.158$ mm^{-1}, $F(000) = 272$, GOF = 1.012. A total of 3435 reflections were collected, of which 1832 were unique ($R_{int} = 0.0152$). $R1/wR2 = 0.0367/0.1020$ for 1623 reflections ($I > 2\sigma(I)$) and 172 parameters. **2a**: $C_8H_{38}B_{16}N_8O_{27}$, $M_r = 851.42$, orthorhombic, *Fdd*2, $a = 14.772(3)$, $b = 64.731(11)$, $c = 6.668(1)$ Å, $V = 6376(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.774$ Mg m^{-3}, $\mu = 0.158$ mm^{-1}, $F(000) = 3504$, GOF = 1.070, Flack parameter $x = 0.3(9)$. A total of 9941 reflections were collected, of which 2826 were unique ($R_{int} = 0.0254$). $R1/wR2 = 0.0409/0.1176$ for 2816 reflections ($I > 2\sigma(I)$) and 267 parameters. CCDC-618071 (**1**) and -618072 (**2a**) contain 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.

[12] Y.-C. Liao, C.-H. Lin, S.-L. Wang, *J. Am. Chem. Soc.* **2005**, *127*, 9986.

[13] D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, **1974**.

[14] a) H. H.-Y. Sung, M. Wu, I. D. Williams, *Inorg. Chem. Commun.* **2000**, *3*, 401; b) M. Wu, T. S.-C. Law, H. H.-Y. Sung, J. Caiab, I. D. Williams, *Chem. Commun.* **2005**, 1827.

[15] E. Y. Silin, V. K. Belskii, G. V. Ozolinsh, *Latv. PSR Zinat. Akad. Vestis Kim. Ser.* **1982**, 375.

[16] a) M. S. Wrighton, D. S. Ginley, D. L. Morse, *J. Phys. Chem.* **1974**, *78*, 2229; b) N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. A. R. R. Kessener, S. C. Moratti, A. B. Holmes, R. H. Friend, *Chem. Phys. Lett.* **1995**, *241*, 89.

[17] T. Jüstel, D. U. Wiechert, C. Lau, D. Sendor, U. Kynast, *Adv. Funct. Mater.* **2001**, *11*, 105, and references therein.