Angewandte Chemie

DOI: 10.1002/anie.200703871

Microporous Materials

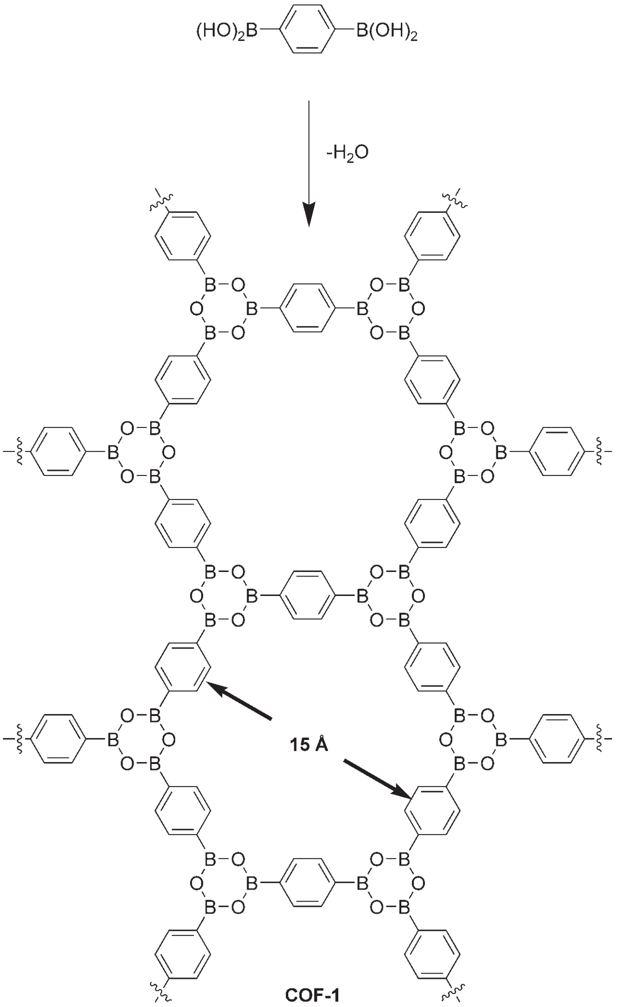
The Next Generation of Shape-Persistant Zeolite Analogues: Covalent Organic Frameworks**

Michael Mastalerz*

boronic acids · microporous materials · nanostructures · polymers · self-organisation

Ten years ago, a Highlight in *Angewandte Chemie International Edition in English* introduced the new, modular concept of metal–organic frameworks (MOFs).[1] Since Yaghi et al. published the first results of this research area in 1995 and introduced the name MOFs for this class of compounds,[2] the number of publications in this area of chemistry has increased exponentially, and will probably continue to do so in the years to come.[3] These zeolite analogues are easily accessible using organic linkers with functional groups that are capable of complexing metal atoms or clusters as connecting units.[4] Because of their defined pore dimensions and high thermal stabilities, these materials have already found broad applications in industrial processes (e.g. catalysis, separation of compound mixtures, crude oil extraction, gas storage) and have started to supplement or substitute zeolites.

Some ten years later, Yaghi et al. described covalent organic frameworks (COFs) for the first time.[5] For these initial systems, the building blocks were 1,4-benzenediboronic acid (BDBA) and hexahydroxytriphenylene (HHTP). Under carefully chosen reaction conditions, BDBA reacts with itself, and the boronic acid moieties condense to planar boroxine rings ($(RB)_3O_3$, Scheme 1).[5] In COFs, these boroxine rings can be seen as analogues of the metal clusters in MOFs. For the synthesis, the selection of the right solvent seems to be important. To foster the formation of a uniform and highly ordered structure, solvents are chosen wherein the reactants are poorly soluble. This approach slows down the reversible condensation. Furthermore, the reactions are carried out in sealed pyrex tubes, again to slow down the reversible process and minimize defects by self-healing. COF-1 was isolated as a microcrystalline substance in high yield. Powder X-ray diffraction patterns reveal a high structural order, whereas single interlayers are stacked in a staggered arrangement. Solvent molecules are enclosed inside the 15-Å-diameter pores and can be removed at 200 °C without collapse of the crystalline structure. COF-1 has a surface area of 711 $m^2 g^{-1}$ and a pore volume of 0.32 $cm^3 g^{-1}$. These values are comparable to those of porous zeolite and carbon-based materials.[4]



Scheme 1. Synthesis of the first covalent organic framework, COF-1.[5]

COF-5 is accessible from BDBA and HHTP under similar reaction conditions and was also synthesized in high yields.[5] The diameters of the pores of this compound are 27 Å and the pore sizes fall within a narrow distribution. These data were supported by the comparison with DFT calculations of model compounds. The layers of the crystalline material are stacked

---

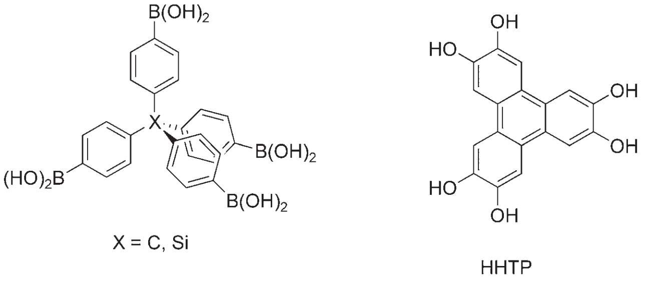
[*] Dr. M. Mastalerz
Ulm University
Organic Chemistry II and Advanced Materials
Albert-Einstein-Allee 11, 89081 Ulm (Germany)
Fax: (+49) 731-502-2840
E-mail: michael.mastalerz@uni-ulm.de

[**] I am grateful to the Deutsche Forschungsgemeinschaft (DFG) for financial support.

in an eclipsed fashion. The specific surface area is 1590 $\mathrm{m^2\,g^{-1}}$, or roughly double that of MCM-41 (Mobile crystalline material 41), which has a comparable pore diameter.[6]

Another representative of this material class is COF-18Å, which was synthesized by the group of Lavigne by condensation of 1,3,5-benzenetriboronic acid (BTBA) and 1,2,4,5-tetrahydroxybenzene (THB).[7] Although the reaction conditions deviate from those in the Yaghi publication, COF-18Å was isolated in excellent yields. This result seems to confirm the concept of slow condensation as a general principle for the generation of highly ordered structures. As the name of the compound suggests, the pore diameter is 18 Å. In comparison with COF-5, COF-18Å has a smaller surface area (1260 $\mathrm{m^2\,g^{-1}}$) and smaller pore volumes (0.29 $\mathrm{cm^3\,g^{-1}}$). To verify the stoichiometric incorporation of both monomer reactants into the framework, COF-18Å was degenerated with KOH in deuterated water. A subsequently recorded ^{1}H NMR spectrum revealed the expected ratio of 3:2 (BTBA/THB).[7]

Recently, Yaghi and co-workers expanded the networking scope to three-dimensional space. Using tetrahedral tetraboronic acids as precursors, 3D frameworks (COF-102, COF-103, COF-105, and COF-108) resulted from condensation or co-condensation with HHTP (Scheme 2 and Figure 1).[8] Although the yields are lower than for the 2D frameworks, the 3D COFs display excellent physicochemical properties. The formation of two different net structures was observed: ctn and bor. Only COF-108 forms the highly porous bor network, and it is, to date, unclear why exclusively this compound crystallizes in the bor structure. The only difference from COF-105 is the central atom of the tetrahedral precursor (Si instead of C). The other three COFs condense in the ctn structure. The COFs 102, 103, and 105 exhibit pore diameters of 8.9, 9.6, and 18.3 Å and densities of 0.41, 0.38, and 0.18 $\mathrm{g\,cm^{3}}$, respectively. Because COF-108 crystallizes in the bor structure, two different types of pores are present, with diameters of 15.2 and 29.6 Å. With a density of 0.17 $\mathrm{g\,cm^{-3}}$, COF-108 is the crystalline material with the lowest density (for comparison: MOF-177 0.42 $\mathrm{g\,cm^{-3}}$, diamond 3.50 $\mathrm{g\,cm^{-3}}$).[9] The surface areas of COFs 102 and 103 (3472 and 4210 $\mathrm{m^2\,g^{-1}}$, respectively) are comparable to that of MOF-177 (4500 $\mathrm{m^2\,g^{-1}}$).



Scheme 2. Monomeric subunits of the three-dimensional COFs 102, 103, 105, and 108.[8]

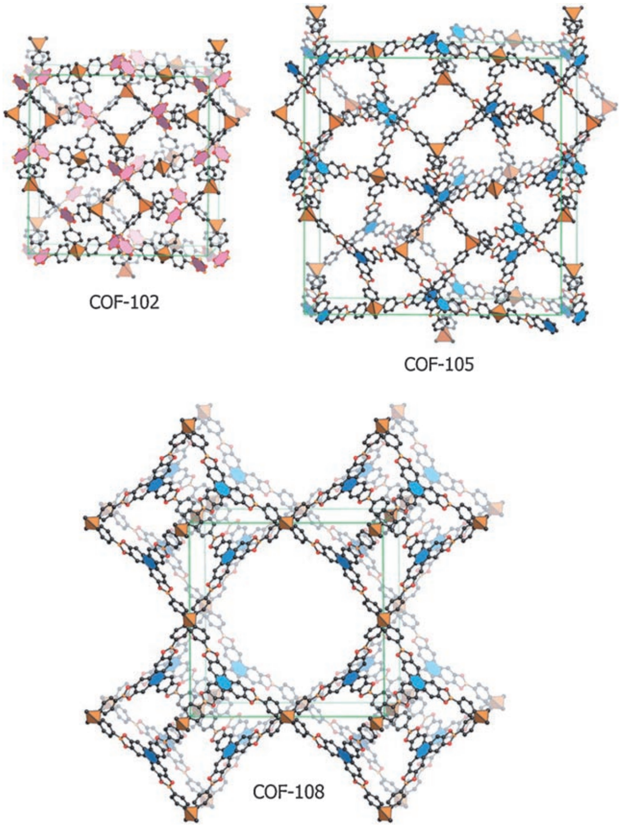
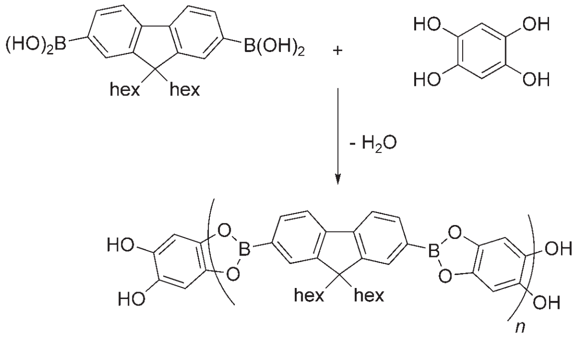


Figure 1. Models of the structures of COFs 102, 105, and 108. Reproduced with permission from reference [8].

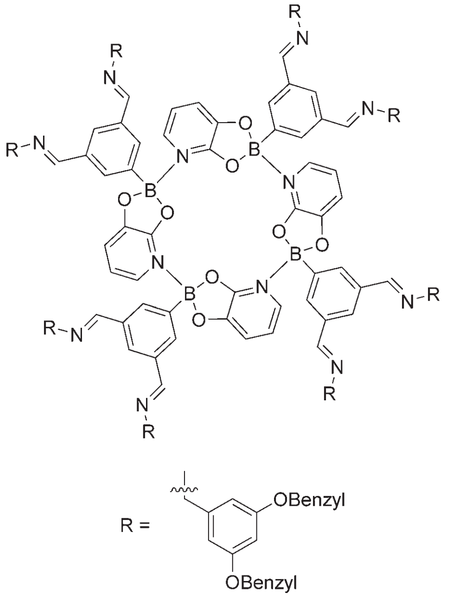


Scheme 3. Blue-emitting polymer based on the condensation of boronic acids and tetraols; Hex = hexyl.[10]

The same method of condensing diboronic acids and tetraols was also used by Lavigne and co-workers to synthesize a new class of blue-emitting conjugated polymers. (Scheme 3).[10] The syntheses of these new materials represent an alternative approach to hitherto existing conjugated polymers. A very similar approach of polymerization of diboronic acids with fluorene or carbazole subunits had been described by Ding and co-workers three years earlier. Dehydration of the precursor mixture led to stable cross-linked polymers. These polymers also showed blue emission and were tested as materials for organic light-emitting diodes (OLEDs).[11] In 1997, Farfán and co-workers used the condensation of boronic acids to the corresponding esters.

By subsequent coordination of the boronic ester functionalities by nitrogen atoms embedded in the backbone, stable macrocyclic boronates were formed.[12]

Severin and co-workers used an analogous method for the generation of macrocyclic structures.[13] Using pyridyl diols and boronic acids containing aldehyde moieties, macrocycles were synthesized as core units for the synthesis of dendrimers (Scheme 4). Depending on the relative position of the nitrogen atom to the hydroxy groups, four- or five-membered rings are accessible. In contrast to Yaghi's strategy, the boronic ester units were additionally coordinated by the pyridyl nitrogen atoms, which results in the ring formation. By subsequent imine condensation reactions of the peripheral aldehyde units with amines, the macrocycles were transformed into dendrimeric compounds. This type of macrocycle synthesis is therefore a new method for the construction of dendrimeric molecules.



Scheme 4. Dendrimers with a macrocyclic borate core.[13]

The above examples have in common that they proceed under thermodynamic control (reversibility of the condensation) and therefore result in highly ordered structures. Recently, Cooper and co-workers demonstrated that it is also possible to access microporous materials with excellent properties under kinetic control.[14] Some of these amorphous polymers have properties comparable to those of COFs (see also the following Highlight).[15]

The high thermostabilities of the COFs up to 500 °C make these compounds potential candidates for use in industrial processes. The low densities and large surface areas up to 4210 $m^2 g^{-1}$ are also properties suitable for potential applications.

These examples demonstrate that the concept of reversible condensation of boronic acids was quickly used in a sophisticated fashion by Yaghi and co-workers to create three-dimensional porous frameworks. This method is also gaining increasing attention in the research areas of polymer and dendrimer chemistry. It will be exciting to see if this new field of chemistry, especially that of the COFs, will establish itself as fast as that of the MOFs.[16] The possibilities are definitely given.

---

[1] C. Janiak, *Angew. Chem.* **1997**, *109*, 1499–1502; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1431–1434.

[2] O. Yaghi, G. Li, H. Li, *Nature* **1995**, *378*, 703–706.

[3] From 1995 to 2000, the number of publication were constantly low (under 15 per year). Since 2001 the number has grown exponentially. So far in 2007, more than 490 contributions on the topic of MOFs have been published.

[4] For reviews, see: a) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388–2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; b) M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; c) O. M. Yaghi, H. L. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474–484; d) S. Kaskel in *Handbook of Porous Solids*, *Vol. 2* (Eds.: F. Schüth, K. S. W. Sing, J. Weitkamp), Wiley-VCH, Weinheim, **2002**, pp. 1190–1249; e) S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276–288.

[5] A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger, O. M. Yaghi, *Science* **2005**, *310*, 1166–1170.

[6] M. Kruk, M. Jaroniec, A. Sayari, *J. Phys. Chem. B* **1997**, *101*, 583.

[7] a) R. W. Tilford, R. Gemmil, H.-C. zur Loye, J. J. Lavigne, *Chem. Mater.* **2006**, *18*, 5296–5301.

[8] H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O'Keeffe, O. M. Yaghi, *Science* **2007**, *316*, 268–272.

[9] a) D. Oron, N. Dudovich, D. Yelin, Y. Silberberg, *Phys. Rev. A* **2002**, *65*, 043408; b) S. H. Lim, A. G. Caster, S. R. Leone, *Phys. Rev. A* **2005**, *72*, 041803.

[10] a) W. Niu, M. D. Smith, J. J. Lavigne, *J. Am. Chem. Soc.* **2006**, *128*, 16466–16467; b) W. Niu, C. O'Sullivan, B. M. Rambo, M. D. Smith, J. J. Lavigne, *Chem. Commun.* **2005**, 4342–4344.

[11] Y. Li, J. Ding, M. Day, Y. Tao, J. Lu, M. D'iorio, *Chem. Mater.* **2003**, *15*, 4936–4943.

[12] a) N. Farfán, H. Höpfl, V. Barba, M. E. Ochoa, R. Santillan, E. Gómez, A. Gutiérrez, *J. Organomet. Chem.* **1999**, *581*, 70–81; b) H. Höpfl, N. Farfán, *J. Organomet. Chem.* **1997**, *547*, 71–77.

[13] a) N. Christinat, R. Scopelliti, K. Severin, *Chem. Commun.* **2004**, 1158–1159; b) N. Christinat, R. Scopelliti, K. Severin, *J. Org. Chem.* **2007**, *72*, 2192–2200.

[14] J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak, A. I. Cooper, *Angew. Chem.* **2007**, *119*, 8728–8732; *Angew. Chem. Int. Ed.* **2007**, *46*, 8574–8578.

[15] C. Weder, *Angew. Chem.* **2008**, *120*, 456–458; *Angew. Chem. Int. Ed.* **2008**, *47*, 448–450.

[16] Note added in proof: Yahgi et al. have now published the structures and properties of three new COFs: COF-6, COF-8, and COF-10, again these have excellent pyhsicochemical properties. A. P. Côté, H. M. El-Kaderi, H. Furukawa, J. R. Hunt, O. M. Yaghi, *J. Am. Chem. Soc.* **2007**, *129*, 12914–12915.