Angewandte Chemie

DOI: 10.1002/anie.200801631

Metal–Organic Frameworks

Postsynthetic Covalent Modification of Metal–Organic Framework (MOF) Materials

*Yu-Fei Song and Leroy Cronin**

encapsulated reactions ·
metal–organic frameworks ·
organic–inorganic hybrid composites ·
porous materials

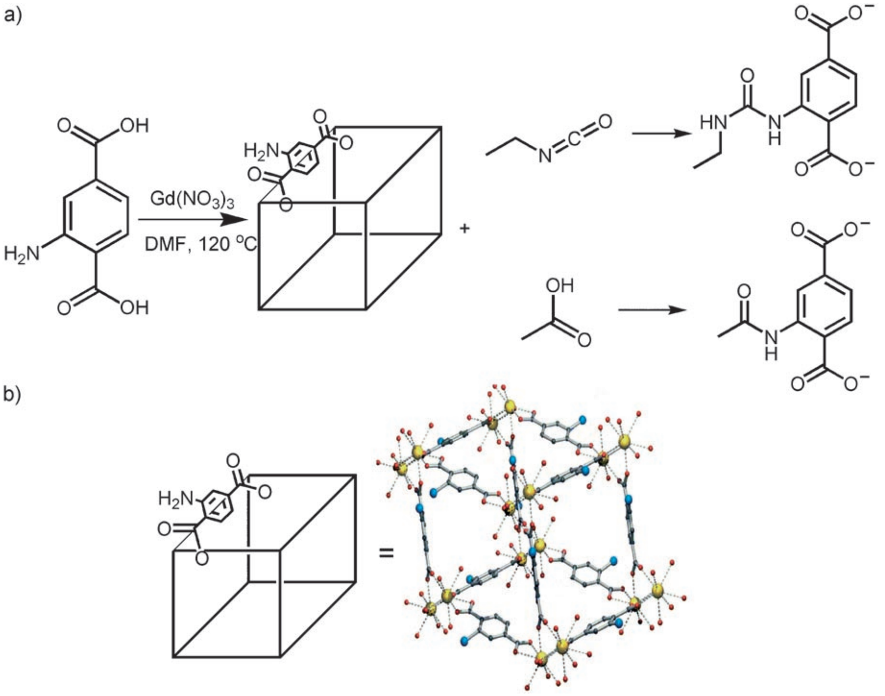
The ability to reliably design, synthesize, and model porous inorganic materials[1] from zeolites and other extended pure inorganic networks to systems comprised of complex inorganic coordination clusters and metal–organic coordination complexes has allowed a fundamental shift from discovery to design in this area of science. This is particularly true in the area of metal–organic materials[2] (MOMs, e.g., metal–organic polyhedra, metal–organic frameworks (MOFs), or coordination polymers) in which many materials have been synthesized and reported as potential platforms for applications in various fields, such as gas storage,[3] ion exchange,[4] catalysis,[5] magnetism,[6] separation,[7] and nonlinear optical materials.[8] To date, there are two principal ways to prepare porous materials: one is focused on the templating method,[9] and the other is based on metal–organic frameworks constructed from molecular building blocks (MBBs). In the former approach, soft templates, such as triblock copolymers and surfactants, or hard templates, such as porous alumina and porous silica, play a crucial role in directing the formation of porous structure. The other approach, which uses metal–organic frameworks (MOFs) to construct porous materials, is also well documented and has been extraordinarily successful.[10] The presence of structure-directing ligands in MOFs means that they are highly amenable to systematic design, both in terms of the structure formed and the tailoring of the properties, structures, and surfaces of the pores present in the material. For example, high-throughput methodologies have been applied successfully to develop a robust synthesis of a zeolitic imidazol framework (ZIF),[11] and the "secondary spillover technique" is able to increase hydrogen storage capacities markedly with the aid of a catalyst that is capable of dissociating H_2 within the materials.[12] Besides exploring new methodologies and searching for new MOFs for effective gas absorption, it is of vital importance and at the same time a great challenge to make MOFs with functionalized pores. The ability to develop well-defined structures with functionalized pores or cavities is of interest, as this will open up the possibility to design hybrid functional materials that will have application in catalysis,[5] as sensors, and as multifunctional materials arising from the incorporation of more than one function within the pore structure.[13] Of course, the key limitation in the development of functional MOFs lies with the introduction of functionality, whilst maintaining the same ability to design and assemble overall framework without unfavorable effects from the presence of the "functional" components. Therefore two possible approaches involve a) the self assembly of the MOF with the functionality already present, and b) the postsynthetic modification of the MOF after self-assembly.

In the latter approach, Gamez et al. have recently reported[14] the crystallographic observation of MOF-based postsynthetic covalent modification inside the pores of a new MOF, in which the amino functional groups oriented inside the pores have been covalently functionalized by reaction with other organic molecules in the cavities without modifying the original three-dimensional framework. This was achieved by the judicious selection of organic linkers which allowed the construction of delicate molecular building blocks (MBBs), and the zeolite-like metal–organic frameworks (ZMOFs) with the desired functionality and directionality. In this case, the small building block, 2-amino-1,4-benzenedicarboxylic acid (N-H_2BDC), which is shown in Scheme 1 and was used in Yaghi's investigation of novel isoreticular MOFs, was employed.[3c] Reaction of this ligand with gadolinium(III) nitrate at 120 °C in DMF leads to a dinuclear gadolinium(III) compound, and both gadolinium(III) ions are connected through four bridging carboxylato moieties of four ligands (Scheme 1). Eight digadolinium building blocks are arranged to form a cube in the crystal structure, and these cubes are further associated to produce an extended three-dimensional octahedral network which features porous channels. Interestingly, the pendant amino groups do not participate in coordination to the dinuclear Gd_2O_7 cluster in this new MOF, which is similar to Yaghi's Zn_4O tetrahedral cluster.[3c] As such, they are readily available for postsynthetic transformation.

The postsynthetic transformation reaction of the amino functionality in this MOF was realized by reaction with ethylisocyanate, and the reaction proceeds as a crystal-to-

---

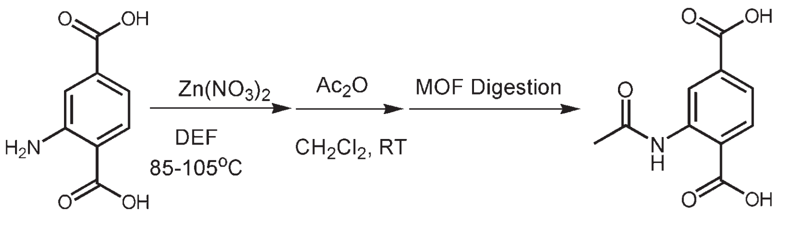
[*] Dr. Y.-F. Song, Prof. Dr. L. Cronin
WestChem, Department of Chemistry
The University of Glasgow, G12 8QQ, Glasgow (UK)
Fax: (+44) 141-330-4888
E-mail: l.cronin@chem.gla.ac.uk
Homepage: http://www.chem.gla.ac.uk/staff/lee/



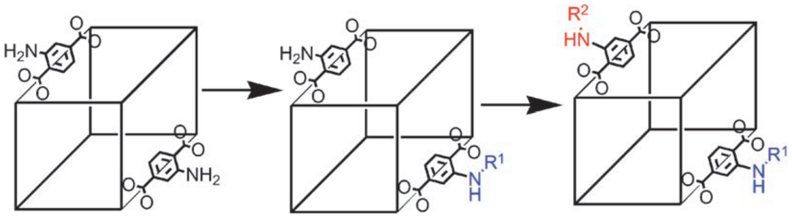
Scheme 1. a) Postsynthetic modification of a gadolinium N-H_2BDC MOF by Gamez et al.: with ethylisocyanate (upper), and acetic acid (lower). b) Correlation of the structure with the schematic representation. Gd yellow, N blue, O red, C gray.[14]

crystal transformation (Scheme 1). Another transformation using the same linker building block was carried out by reaction with acetic acid, which introduces an amide functionality in the MOF observed crystallographically. Thus, using this approach, it is clear that by tethering the organic component to the MOFs, the transformation of original MOFs to new MOFs with different properties can be achieved. This means that the porous compound can be easily and purposely functionalized by its subsequent reaction with a variety of different organic molecules. The significance of the postsynthetic covalent modification of MOF materials lies in the fact that such a unique strategy can be regarded as a powerful, simple, and versatile methodology to prepare functional MOFs in a straightforward way, and at the same time it allows systematic modification of the cavities of porous MOFs. As a result, it should be possible to design a whole range of isostructural MOF networks with a range of chemical functionality, leading to radically different chemical and physical properties compared with the original MOFs.

It should be noted that chemical modification of MOFs in the porous channels was first reported in 2000 by Kim et al.,[5a] in which the N-alkylation of all of the pyridyl groups in the MOFs occurred by adding an excess amount of iodomethane to a suspension of crystalline porous MOF material at room temperature. The pore size was also modulated after N-alkylation of the pyridyl groups, with the pore volume of the MOF shrinking by 14%. The I_3^- anion can be reversibly exchanged with other anions. Furthermore, the presence of the pyridyl group in the channels provides the MOF material with unique opportunities in catalysis. In 2007, Wang and Cohen[15] reported a postsynthetic modification of a MOF framework by using Yaghi's isoreticular IR-MOF-3,[3c] and a variety of chemical analytical methods, including X-ray powder diffraction and spectroscopic techniques, have been utilized to support the direct covalent functionalization (Scheme 2). Wang and Cohen have also made new progress[16] in the exploration of tandem postsynthetic modification of MOFs bearing reactive functional groups, in which each of two modification methods exemplify a highly efficient and controllable approach to the functionalization of MOFs. The results show that more than one chemical reaction and more than one functional group can be introduced into MOF structures by a postsynthetic strategy (Scheme 3). This concept might be applicable to any MOF with sufficient porosity and stability that contains reactive functional groups.



Scheme 2. Postsynthetic modification of the IRMOF-3 MOF by Wang and Cohen. After MOF formation, the framework was modified by acetic anhydride (Ac_2O), and then the MOF was digested to liberate the modified organic units for characterization. DEF = diethylformamide.[15]



Scheme 3. Representation of a tandem modification of a MOF by two different groups R^1 and R^2 by Wang and Cohen.[16]

In summary, recent work has shown that postsynthetic modification of MOFs can be achieved under mild conditions, and this strategy facilitates the generation of new MOFs with new physical and chemical properties that are not observable in robust original MOFs. Programming the architectures in the cavity of the porous material can result in the specific interaction of MOFs with guest molecules, such as hydrogen storage. Given the large number of MOFs reported in the literature, and the vast number of suitable organic reactions available, there must be many tremendous opportunities for developing the systematic postsynthetic modification of MOFs as a general approach to engineer additional functionality, create diversity, and smart materials that can sense, transform certain guests, and change their physical properties. In this respect the assembly of extended solids able to undergo reversible substitution reactions also represents a type of postsynthetic transformation and also provides inspiration for further design.[17] The next great challenge is to develop functional materials based on these derivatized MOFs and even look towards producing MOFs whereby a number of different modifications can be systematically engineered within one framework, thereby increasing functionality and complexity of the material.

---

[1] D. W. Lewis, D. J. Willock, C. R. A. Catlow, J. M. Thomas, G. J. Hutchings, *Nature* **1996**, *382*, 604.

[2] S. Kitagawa, R. Kitaura, S.-i. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334.

[3] a) S.-i. Noro, S. Kitagawa, M. Kondo, K. Seki, *Angew. Chem.* **2000**, *112*, 2161; *Angew. Chem. Int. Ed.* **2000**, *39*, 2081; b) B. Kesanli, Y. Cui, M. Smith, E. Bittner, B. Bockrath, W. Lin, *Angew. Chem.* **2005**, *117*, 74; *Angew. Chem. Int. Ed.* **2005**, *44*, 72; c) M. Eddaoudi, J. Kim, V. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469; d) N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science* **2003**, *300*, 1127.

[4] K. S. Min, M. P. Suh, *J. Am. Chem. Soc.* **2000**, *122*, 6834.

[5] a) J. S. Seo, D. Wand, H. Lee, S. I. Jun, J. Oh, Y. Jeon, K. Kim, *Nature* **2000**, *404*, 982; b) L. Pan, H. Liu, X. Lei, X. Huang, D. H. Olson, N. J. Turro, J. Li, *Angew. Chem.* **2003**, *115*, 560; *Angew. Chem. Int. Ed.* **2003**, *42*, 542; c) B. Kesanli, W. Lin, *Coord. Chem. Rev.* **2003**, *246*, 305; d) C. D. Wu, A. Hu, L. Zhang, W. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 8940; e) C. D. Wu, W. Lin, *Angew. Chem.* **2007**, *119*, 1093; *Angew. Chem. Int. Ed.* **2007**, *46*, 1075.

[6] O. Kahn, *Acc. Chem. Res.* **2000**, *33*, 647.

[7] B. Chen, C. Liang, J. Yang, D. S. Contreras, Y. L. Clancy, E. B. Lobkovsky, O. M. Yaghi, S. Dai, *Angew. Chem.* **2006**, *118*, 1418; *Angew. Chem. Int. Ed.* **2006**, *45*, 1390.

[8] S. Bordiga, C. Lamberti, G. Ricchiardi, L. Regli, F. Bonino, A. Damin, K. P. Lillerud, M. Bjorgen, A. Zecchina, *Chem. Commun.* **2004**, 2300.

[9] a) X. Y. Lai, X. T. Li, W. C. Geng, J. C. Tu, J. X. Li, S. L. Qiu, S. L, *Angew. Chem.* **2007**, *119*, 752; *Angew. Chem. Int. Ed.* **2007**, *46*, 738; b) F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem.* **2006**, *118*, 3290; *Angew. Chem. Int. Ed.* **2006**, *45*, 3216; c) S. M. Abubakar, J. C. Lee, D. M. Marcus, J. O. Ehresmann, J. F. Haw, *J. Phys. Chem. B* **2006**, *110*, 14598; d) J. F. Haw, D. M. Marcus, *Top. Catal.* **2005**, *34*, 41.

[10] a) Y. Liu, V. Ch. Kravtsov, D. A. Beauchamp, J. F. Eubank, M. Eddaoudi, *J. Am. Chem. Soc.* **2005**, *127*, 7266; b) D. F. Sava, V. Ch. Kravtsov, F. Nouar, L. Wojtas, J. F. Eubank, M. Eddaoudi, *J. Am. Chem. Soc.* **2008**, *130*, 3768; c) X. C. Huang, Y. Y. Lin, J. P. Zhang, X. M. Chen, *Angew. Chem.* **2006**, *118*, 1587; *Angew. Chem. Int. Ed.* **2006**, *45*, 1557; d) K. S. Park, Z. Ni, A. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 10186.

[11] R. Ranerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* **2008**, *319*, 939.

[12] a) A. J. Lachawiec, G. S. Qi, R. T. Yang, *Langmuir* **2005**, *21*, 11418; b) Y. W. Li, R. T. Yang, *J. Am. Chem. Soc.* **2006**, *128*, 726; c) Y. W. Li, R. T. Yang, *J. Am. Chem. Soc.* **2006**, *128*, 8136.

[13] a) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040; b) C. Serre, F. Millange, S. Surblé, G. Férey, *Angew. Chem.* **2004**, *116*, 6445; *Angew. Chem. Int. Ed.* **2004**, *43*, 6285.

[14] J. S. Costa, P. Gamez, C. A. Black, O. Roubeau, S. J. Teat, J. Reedijk, *Eur. J. Inorg. Chem.* **2008**, 1551.

[15] Z. Wang, S. M. Cohen, *J. Am. Chem. Soc.* **2007**, *129*, 12368.

[16] Z. Wang, S. M. Cohen, *Angew. Chem.* **2008**, *120*, 4777; *Angew. Chem. Int. Ed.* **2008**, *47*, 4699.

[17] D. Bradshaw, J. E. Warren, M. J. Rosseinsky, *Science* **2007**, *315*, 977.