Communication

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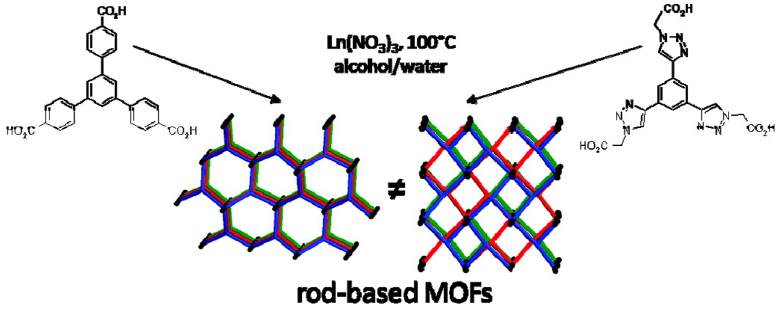

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An Illustration of the Limit of the Metal Organic Framework's Isoreticular Principle Using a Semirigid Tritopic Linker Obtained by "Click" Chemistry

Thomas Devic,* Olivier David,* Marion Valls, Jérôme Marrot, François Couty, and Gérard Férey*

Institut Lavoisier, CNRS UMR 8180, Université de Versailles, Saint-Quentin-en-Yvelines, 45 avenue des Etats-Unis, 78035 Versailles cedex, France

Received June 18, 2007; E-mail: devic@chimie.uvsq.fr

The search for very large pores[1] in metal organic frameworks (MOFs) is currently topical,[2] due to the unprecedented properties they generate in adsorption and now in drug delivery.[3] The isoreticular principle[4] is one way to tune the size of the pores by acting on the length of the rigid linker, keeping constant the inorganic part. It was applied on a few series based either on molecular[4−7] or 1-D[8,9] inorganic parts. We recently prepared a porous MOF (denoted MIL-103, MIL = Materials Institut Lavoisier) based on an extended tritopic linker (1,3,5-benzenetrisbenzoate) and lanthanide chains.[10] In order to see the effect of the addition of nitrogen lone pairs and small flexible endings at the periphery of the rigid core on the sorption properties of this structure type,[11] we prepared a new trigonal nitrogen-rich linker[12] including 1,2,3-triazole rings, which was obtained by a triple Huisgen 1,3-dipolar cycloaddition. This reaction was described as a case example of "click" chemistry[13] and is currently widely used in various fields of chemistry,[14] ranging from bio-related applications to material science or coordination chemistry. The key features of this reaction (high yield, reasonably easy scale-up, etc.) prompted us to use it for the synthesis of new nitrogen-rich linkers on the multigram scale, a prerequisite to further potential applications of the related MOFs. This paper describes the synthesis of a new nitrogen-rich tricarboxylate linker obtained by "click" chemistry, the preparation, and characterization of an open metal organic framework (hereafter denoted MIL-112) using this linker.

{4-[3,5-Bis-(1-carbonylmethyl-1*H*-[1,2,3]triazol-4-yl)-phenyl]-[1,2,3]triazol-1-yl}acetic acid (later denoted $\mathbf{L}H_3$) was obtained in two steps starting from 1,3,5-triethynylbenzene[15] and azidoglycine ethylester[16] on the 10 g scale, using the standard "click" conditions[13b] (Scheme 1 and Supporting Information for details).

Using reaction conditions identical to those of MIL-103,[10] a crystalline phase appeared with light lanthanides (Ln = La−Nd). Optimized conditions led to pure powders and to single crystals suitable for X-ray diffraction (see Supporting Information).

MIL-112 is formulated $La(\mathbf{L})(H_2O)_2 \cdot 6H_2O$ from X-ray[17] and chemical analyses. The 10-folded La^{III} ions (eight carboxylate oxygen atoms and two terminal H_2O) connect to each other through bridging μ_2-oxygen atom to define rods of edge-sharing $[LaO_{10}]$ polyhedra running along the *c*-axis. Each tritopic linker $\mathbf{L}^{3-}$ is bonded to three inorganic chains, defining two types of small channels developing along the *c* direction, both filled with free water molecules (Figure 1).

MIL-103 and -112 have close formulations $Ln(\mathbf{L})(H_2O)_x \cdot (solv)_y$ ($x = 1$, solv = H_2O (MIL-103) and $x = 2$, solv = $C_6H_{11}OH$ (MIL-112)), and both structures are built up from chains of edge-sharing $[LnO_{9/10}]$ polyhedra, owing to similar experimental conditions. The only difference concerns the coordination modes of the carboxylate groups (two chelating bridging and one bridging groups in MIL-103 and two chelating bridging and one chelating carboxylate groups in MIL-112).

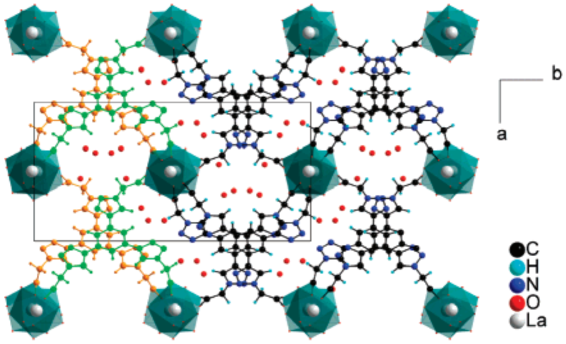
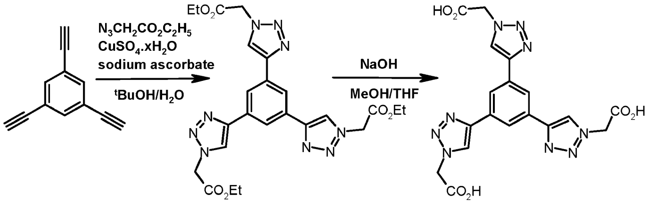


Figure 1. View of MIL-112 along the *c*-axis, showing the two types of channels, both containing free water molecules. On the left side, successive layers of linkers are colored in green and orange.

Scheme 1. Synthesis of $\mathbf{L}H_3$



The parallel rods act as scaffolds for both 3-D structures.[18] In terms of projected 2-D net, the highly porous MIL-103 is hexagonal 6^3 with a perfect AAA stacking of the layers, the linker having a strict C_3-symmetry; MIL-112 corresponds to a 4^4 net despite the tritopic character of the linkers. Both the pentagonal triazole rings and the flexibility of the methylene groups are responsible of the difference. The linkers are T-shaped, with different orientations, and the ABA staggered stacking defines in each layer four- (square) and eight-membered (rectangle) rings, thus preventing the formation of large pores (Figure 2).

This example illustrates that, in rod-based MOFs,[9] even if the core of the ligand remains rigid, the introduction of some flexibility on the shell drastically changes the structure. Therefore, the isoreticular principle here no longer applies and remains valid only for strictly rigid ligands which impose strong geometric constraints to the structure, as already pointed out by Chae et al. in the case of trigonal linkers and molecular inorganic SBUs.[19] The free rotation of the carboxylate function around the methylene group does not force a strict C_3-symmetry and allows other configurations, governed by lattice energy minima, to happen.

By heating under dioxygen, MIL-112 shows two weight losses at low temperature (15 and 20% (experimental as calculated) at 50 and 160 °C, respectively; see Figure 3). They correspond to the evacuation of the water molecules of the tunnels and further to the formation of the fully dehydrated Ln(**L**). The structure collapses at 300 °C to finally yield La_2O_3 at higher temperature.

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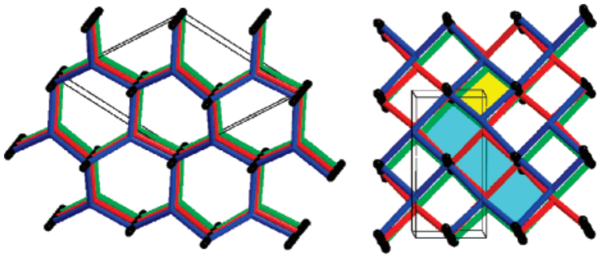

Figure 2. Comparison of the network topologies in MIL-103 (left) and MIL-112 (right). In black: lanthanide chains. Three successive layers of linkers (in blue, red, and green, respectively) are pictured. Square and rectangle rings in MIL-112 are highlighted in yellow and light blue, respectively.

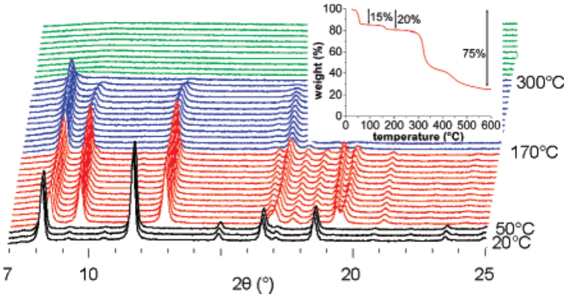

Figure 3. Thermal behavior of MIL-112. Thermodiffractogram performed under air between 20 and 400 °C. In black: La(**L**)$(H_2O)_2$•$6H_2O$; red: La(**L**)$(H_2O)_2$; blue: La(**L**); green: amorphous. Inset: Thermogravimetric analysis performed under O_2 between room temperature and 600 °C.

As shown by X-ray thermodiffractometry (Figure 3), the title solid Ln(**L**)$(H_2O)_2$•$6H_2O$ phase is stable up to 50 °C. Above, Ln(**L**)$(H_2O)_2$ appears. Its X-ray pattern is new and almost invariant until 170 °C. Its indexation proves that its cell parameters are close to those of MIL-112[17] except for the *b*-axis which contracts by 15%.

The N_2 adsorption isotherms were performed at 77 K on MIL-112 for La(**L**)$(H_2O)_2$ and La(**L**) after vacuum activation at 25 and 150 °C. Whatever the conditions, almost no microporosity relative to nitrogen was observed (BET surfaces are 20 and 28 $m^2 \cdot g^{-1}$). This might relate to the contraction, induced by the linker intrinsic flexibility, which prevents the achievement of any permanent porosity. Rehydration is slowly reversible (see Supporting Information), but attempts to re-open the network upon gas pressure (CO_2, $P = 11$ bar) were unsuccessful.

To conclude, MIL-112, which contains a new tritopic "click" carboxylate linker, illustrates the limits of the isoreticular principle when some flexibility is introduced, even when infinite 1-D inorganic SBUs are used. This flexibility prevents the formation of a network isotypic with the porous MIL-103.

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Supporting Information Available: Full synthetic method, characterizations, and the cif file for (La(**L**)$(H_2O)_2$•$6H_2O$) are available. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Férey, G.; Cheetham, A. K. *Science* **1999**, *283*, 1125−1126.
(2) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Surblé, S.; Dutour, J.; Margiolaki, I. *Science* **2005**, *309*, 2040−2043.
(3) Horcajada, P.; Serre, C.; Vallet-Regi, M.; Seban, M.; Taulelle, F.; Férey, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 5974−5978.
(4) (a) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319−330. (b) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469−472.
(5) Surblé, S.; Serre, C.; Mellot-Draznieks, C.; Millange, F.; Férey, G. *Chem. Commun.* **2006**, 284−286.
(6) (a) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148−1150. (b) Ma, S.; Sun, D.; Ambrogio, M.; Fillinger, J. A.; Parkin, S.; Zhou, H. C. *J. Am. Chem. Soc.* **2007**, *129*, 1858−1859.
(7) Lin, X.; Jia, J.; Zhao, X.; Thomas, K. M.; Blake, A. J.; Walker, G. S.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7358−7364.
(8) (a) Loiseau, T.; Serre, C.; Huguenard, C.; Fink, G.; Taulelle, F.; Henry, M.; Bataille, T.; Férey, G. *Chem.*−*Eur. J.* **2004**, *10*, 1373−1382. (b) Loiseau, T.; Mellot-Draznieks, C.; Muguerra, H.; Ferey, G.; Haouas, M.; Taulelle, F. *C. R. Chim.* **2005**, *8*, 765−772.
(9) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 1504−1518.
(10) Devic, T.; Serre, C.; Audebrand, N.; Marrot, J.; Ferey, G. *J. Am. Chem. Soc.* **2005**, *127*, 12788−12789.
(11) Kitagawa, S.; Noro, S.; Nakamura, T. *Chem. Commun.* **2006**, 701−707.
(12) For a recent example of such linker, see: Sun, D.; Ma, S.; Ke, Y.; Collins, D. J.; Zhou, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 3896−3897.
(13) (a) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004−2021. (b) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596−2599.
(14) (a) Lutz, J.-F. *Angew. Chem., Int. Ed.* **2007**, *46*, 1018−1025. (b) Rohde, R. D.; Agnew, H. D.; Yeo, W. S.; Bailey, R. C.; Heath, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 9518−9525. (c) Fleming, D. A.; Thode, C. J.; Williams, M. E. *Chem. Mater.* **2006**, *18*, 2327−2334. (d) Suijkerbuijk, B. M. J. M.; Aerts, B. N. H.; Dijkstra, H. P.; Lutz, M.; Spek, A. L.; van Koten, G.; klein Gebbink, R. J. M. *Dalton Trans.* **2007**, 1273−1276.
(15) (a) Gaab, K. M.; Thompson, A. L.; Xu, J.; Martinez, T. J.; Bardeen, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 9288−9289. (b) Wright, A. T.; Zhong, Z.; Anslyn, E. V. *Angew. Chem., Int. Ed.* **2005**, *44*, 5679−5682.
(16) (a) Tietze, L. F.; Major, F. *Eur. J. Org. Chem.* **2006**, 2314−2321. (b) Hooper, N.; Beeching, L. J.; Dyke, J. M.; Morris, A.; Ogden, J. S.; Dias, A. A.; Costa, M. L.; Barros, M. T.; Cabral, M. H.; Moutinho, A. M. C. *J. Phys. Chem. A* **2002**, *106*, 9968−9975.
(17) Single crystal data for La[$C_{18}H_{12}N_9O_6$][H_2O]$_2$•6(H_2O): monoclinic, space group $P2_1/c$ (No. 14), $a = 12.401(3)$ Å, $b = 24.897(5)$ Å, $c = 8.779(2)$ Å, $\beta = 92.27(3)°$, $V = 2708.5(9)$ A^3, $Z = 4$, $D_{calcd} = 1.799$ $g \cdot cm^{-3}$, $T = 250$ K, $R1 = 0.0815$, $wR2 = 0.1284$ for all data; $R1 = 0.0442$, $wR2 = 0.1006$ for 5327 observed data ($I > 2\sigma(I)$) with 0 restraints and 379 parameters. Powder data for La[$C_{18}H_{12}N_9O_6$][H_2O]$_2$: monoclinic, space group $P2_1/c$ (No. 14), $a = 12.373(1)$ Å, $b = 21.258(2)$ Å, $c = 8.7033(7)$ Å, $\beta = 97.987(4)°$, $V = 2267.0$ A^3.
(18) O'Keeffe, M.; Andersson, S. *Acta Crystallogr.* **1977**, *A33*, 914−923.
(19) Chae, H. K.; Siberio-Pérez, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.; Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523−527.

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