Angewandte Chemie

DOI: 10.1002/anie.200901964

Porous Materials

A Highly Connected Porous Coordination Polymer with Unusual Channel Structure and Sorption Properties**

Yue-Biao Zhang, Wei-Xiong Zhang, Fei-Yue Feng, Jie-Peng Zhang, and Xiao-Ming Chen**

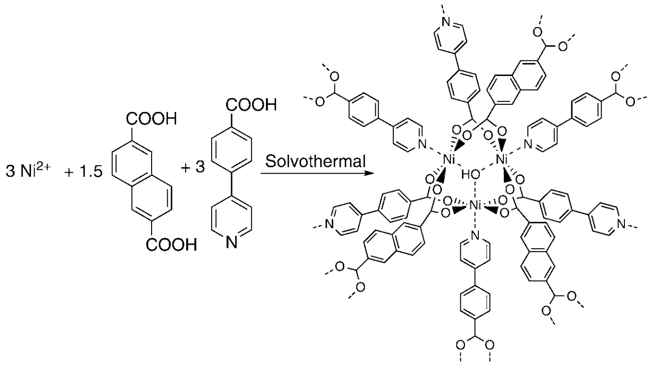
As a burgeoning field in the last two decades, porous coordination polymers (PCPs) have attracted intense scientific interest owing to the aesthetics of diverse network structures and the corresponding novel phenomena and functionalities.[1] The employment of network topology is helpful to analyze, identify, and systematize PCPs, and even affords blueprints for constructing new reticular architectures.[2,3] Simple and highly symmetric networks are very important in the crystal engineering of PCPs. Although uniform or uninodal, low-connected networks have been extensively encountered, simple, highly connected ones have been scarcely realized, except for a few instances of 8-, 12-, and 14-connected prototypes.[4]

Considerable effort has been devoted to extending the structural library of PCPs. Among various synthetic strategies, the utilization of metal–carboxylate frameworks (MCFs) for constructing PCPs represents a mainstream method. The network topologies of MCFs can be readily controlled by well-defined metal–carboxylate clusters, which serve as structurally directing secondary building units (SBUs). Furthermore, the pore size and surface characteristics can also be easily tailored by modification of the carboxylate ligands.[5]

The well-known $M_2(O_2CR)_4L_2$ (M = Cu, Zn, etc.; L = terminal ligand), $Zn_4O(O_2CR)_6$, and $M_3(\mu_3\text{-}O)(O_2CR)_6L_3$ (M = Cr, Fe, Ni, Co, etc.) have been widely utilized as square-planar, octahedral, and trigonal prismatic[6] SBUs by substitution of the available carboxylate groups. Actually, the terminal L sites of these clusters can also be ligated by bridging ligands to furnish higher-connected nodes. As $M_2(O_2CR)_4L_2$ nodes have been widely used as octahedral, six-connected nodes, the tricapped trigonal prismatic, nine-connected $M_3(\mu_3\text{-}O)(O_2CR)_6L_3$[7] should be of great interest since it satisfies the node geometry of the simplest (uninodal, two kinds of edges, high symmetry $I\bar{4}3m$) nine-connected topology ncb, which has only been theoretically predicted but not yet observed.

The difficulty of connecting $M_3(\mu_3\text{-}O)(O_2CR)_6L_3$ into an ncb framework arises from a key requirement: the ditopic ligands must contain a 2:1 molar ratio of carboxylate and pyridyl (or similar monodentate) groups. Obviously, a single kind of ditopic ligand can never fulfill this requirement. Alternatively, a combination of ditopic dicarboxylate and bipyridine in 2:1 ratio or ditopic dicarboxylate and pyridyl carboxylate in 1:2 ratio must be used. Since ditopic dicarboxylate and bipyridine is known to prefer α-Po networks based on octahedral $M_2(O_2CR)_4L_2$ nodes, we tested some potential combinations of ditopic dicarboxylate and pyridyl carboxylate ligands.

By using naphthalene-2,6-dicarboxylate (ndc) and 4-(pyridin-4-yl)benzoate (pba) as mixed linkers, a robust PCP $[Ni^{II}_2Ni^{III}(\mu_3\text{-}OH)(pba)_3(ndc)_{1.5}]\cdot 9.5\,DMA\cdot 8.5\,H_2O$ (MCF-19; DMA = *N,N′*-dimethylacetylamide) with ncb topology was obtained (Scheme 1). The formula and oxidation states of the metal ions were determined by X-ray single-crystal diffraction, thermogravimetry, elemental analysis, magnetic susceptibility measurement, and bond valence sum calculation (see the Supporting Information).



Scheme 1. Construction of a structural unit of the uninodal, nine-connected network of MCF-19 by mixed linear organic ligands and the hydroxy-centered trinuclear nickel cluster.

Crystallizing in the space group *I*23, MCF-19 presents a highly symmetric structure. The planar $Ni_3(\mu_3\text{-}OH)$ cluster (Ni–O = 1.982(2) Å, Ni-O-Ni = 119.95(1)°) with C_3 symmetry is encapsulated by six carboxylate groups (three from pba and three from ndc, Ni–O = 2.037(2)–2.066(2) Å) and three pyridyl groups of pba (Ni–N = 2.076(2) Å) to form a tricapped trigonal prismatic $Ni_3(\mu_3\text{-}OH)(O_2CR)_6L_3$ SBU, which is rare but has been reported in PCPs.[7a] This SBU is connected by three ndc and six pba units into an unprecedented, uninodal nine-connected net, ncb.[3a] Up to now, there has

---

[*] Y.-B. Zhang, W.-X. Zhang, F.-Y. Feng, Dr. J.-P. Zhang, Prof. X.-M. Chen
MOE Key Laboratory of Bioinorganic and Synthetic Chemistry
School of Chemistry & Chemical Engineering
Sun Yat-Sen University, Guangzhou 510275 (P. R. China)
Fax: (+86) 20-8411-2245
E-mail: zhangjp7@mail.sysu.edu.cn
cxm@mail.sysu.edu.cn
Homepage: http://ce.sysu.edu.cn/cxm/
http://ce.sysu.edu.cn/cxm/

[**] This work was supported by NSFC (No. 20821001 and 20531070) and the "973 Project" (2007CB815302).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200901964.

only been one reported case (ncd) for the uninodal nine-connected topology.[8]

Comparison of the real network structure and the ideal geometry of ncb gives useful information. The network structure of MCF-19 possesses the same cubic symmetry as ncb, thus indicating geometry compatibility between the building blocks and topology. The lengths of ndc and pba are almost identical, as predicted by the topology. However, the geometry of the nine-connected node of ncb is clearly distorted from an ideal tricapped trigonal prism (Figure 1 a).

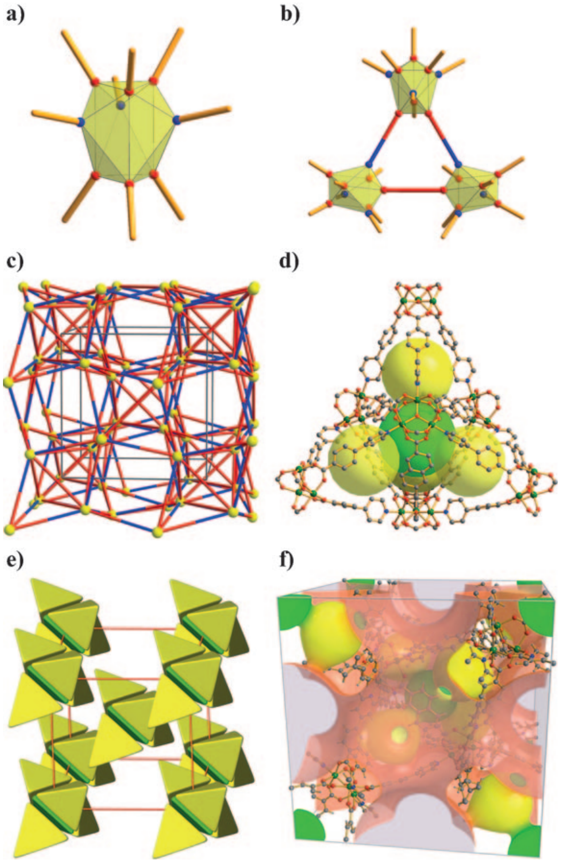


Figure 1. a) Geometry of the nine-connected node in an ideal ncb net (red: prismatic vertex, blue: capped vertex); b) two kinds of linking between nodes; c) ncb net built up by the nine-connected node with two kinds of edges; d) the triakis tetrahedron consists of one tetrahedral cage (green) and four trigonal-pyramidal cages (yellow); e) the *I*-centered cubic periodic array of the triakis tetrahedra; f) connectivity between the NbO-type channel system and cavities in the triakis tetrahedra.

Detailed analysis reveals that the framework distortions occur at the long organic ligands rather than the SBUs (see the Supporting Information), which indicates that the ncb network can hardly be constructed by the same SBUs with shorter or less flexible ligands, whereas longer and more flexible linkers would be suitable for building an isoreticular PCP with larger pores and less tensile force. Notably, the nine-connected nodes in ncb are connected in two ways: prismatic vertex to prismatic vertex and capped vertex to prismatic vertex (Figure 1 b,c), which are mimicked by a dicarboxylate ndc and a pyridyl carboxylate pba, respectively. The absence of a capped vertex to capped vertex connection in ncb indicates that ncb cannot be constructed by the combination of ditopic dicarboxylate and bipyridine.

MCF-19 contains tetrahedral cages and trigonal-pyramidal cages in the ratio of 1:4 (Figure 1 d). The tetrahedral cage is enclosed by four SBUs and six ndc units, with an internal free diameter of about 9.3 Å and window diameter of about 4.7 Å. The trigonal-pyramidal cage is enclosed by four SBUs, three ndc, and three pba units, with internal free diameter of about 8.6 Å. A face of the trigonal-pyramidal cage is also one for the tetrahedral cage (surrounded by three ndc molecules), while the other three faces have window diameters of approximately 4.2 Å. Each tetrahedral cage is capped by four trigonal-pyramidal cages to generate a triakis tetrahedron.[9] The overall structure can be described as a periodic array of triakis tetrahedra in an *I*-centered cubic fashion (Figure 1 e). By sharing the eight trinuclear SBUs, each triakis tetrahedron is connected to eight adjacent ones in a cusp-to-umbilicus fashion, which generates a CsCl net. The calculated solvent-accessible void of the triakis tetrahedra is about 21.2 % of the volume of the whole crystal. Out of the CsCl network of triakis tetrahedra, there is an NbO-type (dual net of CsCl) channel system with large cavities of diameter about 12.4 Å and apertures of about 8.4 Å (Figure 1 f), which occupies approximately 47.3 % of the volume of the whole crystal. Fascinatingly, this large channel is surrounded by numerous cavities of the triakis tetrahedra with small passages (ca. 4.2 Å, the small aperture of the trigonal-pyramidal cage).

Therefore, the overall channel system consists of three types of cavities that are connected through three types of small passages, thus leading to an exceptional channel system that might cause complicated and interesting adsorption phenomena. The calculated solvent-accessible void of the whole crystal reaches a volume of 68.5 %, which implies a promisingly high sorption capacity since the density of the guest-free framework is only 0.637 $\mathrm{g\,cm^{-3}}$.

MCF-19 can be readily synthesized in high yield. The phase purity of the as-synthesized sample was confirmed by powder X-ray diffraction. Thermogravimetric analysis (TGA) of the as-synthesized sample showed a sharp weight loss below 150 °C and a slight weight loss in the range of 150 to 250 °C, which is attributed to the removal of high-boiling-point guest molecules such as DMA. Although TGA did not show further weight loss below 320 °C, thermodiffractometry indicated that the framework of MCF-19 is only stable up to 250 °C, which might be attributed to the internal tension of the framework. Nevertheless, the thermal stability of MCF-19 is comparable to that of the prototypical PCPs, such as HKUST-1 and CPL-1.[10] To achieve milder activating conditions, the included solvent was exchanged by dichloromethane until the characteristic IR peak of DMA was eliminated. TGA of the solvent-exchanged sample exhibits a complete weight loss below 100 °C.

To characterize the porosity of MCF-19, solvent-exchanged MCF-19 was degassed under high vacuum at 90 °C, and sorption isotherms for N_2 at 77 K and CO_2 at 195 K were measured (Figure 2). The N_2 sorption represents a

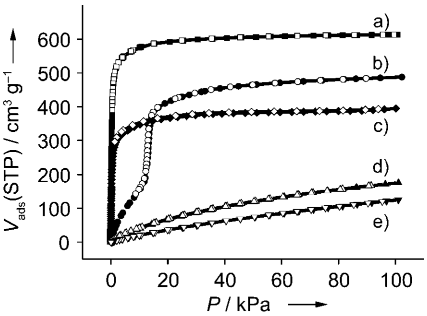


Figure 2. Gas sorption isotherms of guest-free MCF-19: a) N_2 at 77 K; b) CO_2 at 195 K; c) N_2 at 77 K (partially degassed at 80 °C); d) H_2 at 77 K; e) CH_4 at 195 K.

typical reversible type I isotherm and very high adsorption capacity. Based on the N_2 isotherm, the apparent Langmuir and Brunauer–Emmett–Teller (BET) surface areas of MCF-19 were estimated to be 2667 and 2316 $m^2 g^{-1}$, respectively. The pore volume of MCF-19 was calculated to be 0.95 $cm^3 g^{-1}$ based on the Dubinin–Astakhov equation, which is close to that predicted from the crystal structure. These values are comparable to those of the highly porous PCPs MOF-500 and MIL-100, which are also based on the trinuclear SBUs.[11]

As a biporous material, the sorption behavior of some gases could visualize the detail of the heterogeneity of the pores. The CO_2 sorption of MCF-19 at 195 K features an obvious two-step behavior. Applying the Langmuir equation to the CO_2 isotherm, the saturation sorption amounts of the two steps were estimated to be 352 and 510 cm^3(STP) g^{-1} (STP = standard temperature and pressure), respectively, which are a satisfactory match to the calculated pore volumes of the NbO channel (47.3 %) and the whole channel system (68.5 %). This finding implies that at low P/P_0 the adsorption should mainly occur in the NbO channel, and the triakis tetrahedra cavities are only available at relatively high P/P_0. Consequently, the apparent Langmuir surface areas of the NbO channel and the whole pore can be estimated as 2044 and 2957 $m^2 g^{-1}$, respectively, which also illustrates the high porosity of MCF-19. The gated sorption behavior can be attributed to the small apertures between the NbO channel and the triakis tetrahedra cavities. Surprisingly, this phenomenon is observed for CO_2 at 195 K rather than N_2 at 77 K, which indicates that the difference in diffusion between the two gases can be better elucidated by their molecular sizes (CO_2 3.4, N_2 3.1 Å) rather than the kinetic diameters (CO_2 3.3, N_2 3.6 Å). Interestingly, the small apertures of MCF-19 may be readily blocked by guest molecules. When the sample was insufficiently activated at 80 °C, MCF-19 showed a saturation N_2 sorption level only about two-thirds of that for the fully activated sample, which implies that the small apertures were blocked by the residual guest molecules at 77 K.

Furthermore, MCF-19 can also adsorb considerable amounts of hydrogen and methane. The hydrogen uptake of MCF-19 at 77 K and 1 atm reaches 175 $cm^3 g^{-1}$ (1.56 wt %), higher than that for zeolites and most activated carbons and comparable to those for MOF-5, MOF-177, IRMOF-6, IRMOF-8, and PCN-9.[12] The methane uptake of MCF-19 at 195 K and 1 atm is 125 $cm^3 g^{-1}$ (80 cm^3(STP) cm^{-3}), which indicates moderate methane affinity.[5b,13]

In summary, by using a suitable combination of transition-metal ion, dicarboxylate, and pyridyl carboxylate, we have constructed a novel uninodal nine-connected network, which exhibits not only a unique framework structure but also an interesting biporous intersecting-channel system. As a result of its novel structure and unusual sorption behavior, the material reported here may serve as a prototype for the construction of new porous materials with improved sorption performance.

Experimental Section

MCF-19: A solution of $Ni(NO_3)_2 \cdot 7H_2O$ (0.087 g, 0.3 mmol) in methanol (5 mL) was added to a mixture of H_2ndc (0.033 g, 0.15 mmol), Hpba (0.060 g, 0.3 mmol), and NaOH (0.028 g, 0.7 mmol) in DMA (20 mL) under stirring and heating in a 50 mL round-bottomed flask on a water bath. The green suspension was then sealed in a 60 mL Teflon-lined stainless steel vessel and heated to 160 °C for 3 days. Upon cooling to room temperature at a rate of 5 °C h^{-1}, cubic green crystals were obtained (ca. 0.130 g, 65 % yield based on Ni).

Crystal data of MCF-19: cubic $I23$ (No. 197), $a = 28.482(2)$ Å, $V = 23105(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 0.637$ g cm^{-3}, $T = 103(2)$ K, $R_{int} = 0.072$, final $R_1 = 0.0427$ ($I \geq 2\sigma$), $wR_2 = 0.1105$ (all data), $S = 1.003$, Flack parameter = 0.11(2). The intensity data were recorded on a Bruker SMART Apex CCD system with MoK_α radiation ($\lambda = 0.71073$ Å) at 293 K. CCDC 720382 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: April 13, 2009

Keywords: cage compounds · coordination polymers · crystal engineering · metal–organic frameworks · porous materials

---

[1] a) G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191–214; b) M. Dincă, J. R. Long, *Angew. Chem.* **2008**, *120*, 6870–6884; *Angew. Chem. Int. Ed.* **2008**, *47*, 6766–6779.

[2] a) A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Wiley Interscience, New York, **1977**; b) N. Ockwig, O. D. Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176–182; c) L. Öhrström, K. Larsson, *Molecule-Based Materials: The Structural Network Approach*, Elsevier, Amsterdam, **2005**.

[3] a) M. O'Keeffe, O. M. Yaghi, S. Ramsden, *Reticular Chemistry Structure Resource (RCSR)*, **2007**, http://rcsr.anu.edu.au; b) S. Ramsden, V. Robins, S. T. Hyde, S. Hungerford, *EPINET: Euclidean patterns in non-Euclidean tilings*, **2006**, http://epinet.anu.edu.au; c) V. A. Blatov. **2007**, http://www.topos.ssu.samara.ru.

[4] a) R. J. Hill, D.-L. Long, N. R. Champness, P. Hubberstey, M. Schröder, *Acc. Chem. Res.* **2005**, *38*, 335–348; b) D. Li, T. Wu, X.-P. Zhou, R. Zhou, X.-C. Huang, *Angew. Chem.* **2005**, *117*, 4247–4250; *Angew. Chem. Int. Ed.* **2005**, *44*, 4175–4178; c) X.-M. Zhang, R.-Q. Fang, H.-S. Wu, *J. Am. Chem. Soc.* **2005**, *127*, 7670–7671; d) A. J. Cairns, J. A. Perman, L. Wojtas, V. Ch. Kravtsov, M. H. Alkordi, M. Eddaoudi, M. J. Zaworotko, *J. Am. Chem. Soc.* **2008**, *130*, 1560–1561; e) Z.-M. Hao, R.-Q. Fang, H.-S. Wu, X.-M. Zhang, *Inorg. Chem.* **2008**, *47*, 8197–8203.

[5] a) O. M. Yaghi, M. O'Keeffe, N. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714; b) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469–472.

[6] a) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040–2043; b) A. C. Sudik, A. P. Côté, O. M. Yaghi, *Inorg. Chem.* **2005**, *44*, 2998–3000.

[7] a) J.-H. Jia, X. Lin, C. Wilson, A. J. Blake, N. R. Champness, P. Hubberstey, G. Walker, E. J. Cussen, M. Schröder, *Chem. Commun.* **2007**, 840–842; b) X.-M. Zhang, Y.-Z. Zheng, C.-R. Li, W.-X. Zhang, X.-M. Chen, *Cryst. Growth Des.* **2007**, *7*, 980–983.

[8] J. J. Morris, B. C. Noll, K. W. Henderson, *Chem. Commun.* **2007**, 5191–5193.

[9] http://mathworld.wolfram.com/TriakisTetrahedron.html.

[10] a) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148–1150; b) M. Kondo, T. Okubo, A. Asami, S. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka, K. Seki, *Angew. Chem.* **1999**, *111*, 190–193; *Angew. Chem. Int. Ed.* **1999**, *38*, 140–143.

[11] a) A. C. Sudik, A. P. Côté, A. G. Wong-Foy, M. O'Keeffe, O. M. Yaghi, *Angew. Chem.* **2006**, *118*, 2590–2595; *Angew. Chem. Int. Ed.* **2006**, *45*, 2528–2533; b) G. Férey, C. Serre, F. Millange, C. Mellot-Draznieks, S. Surblé, J. Dutour, I. Margiolaki, *Angew. Chem.* **2004**, *116*, 6456–6461; *Angew. Chem. Int. Ed.* **2004**, *43*, 6296–6301.

[12] D. J. Collins, H.-C. Zhou, *J. Mater. Chem.* **2007**, *17*, 3154–3160.

[13] a) V. C. Menon, S. Komarneni, *J. Porous Mater.* **1998**, *5*, 43–58; b) S. Noro, S. Kitagawa, M. Kondo, K. Seki, *Angew. Chem.* **2000**, *112*, 2161–2164; *Angew. Chem. Int. Ed.* **2000**, *39*, 2081–2084; c) S.-Q. Ma, D.-F. Sun, J. M. Simmons, C. D. Collier, D.-Q. Yuan, H.-C. Zhou, *J. Am. Chem. Soc.* **2008**, *130*, 1012–1016.