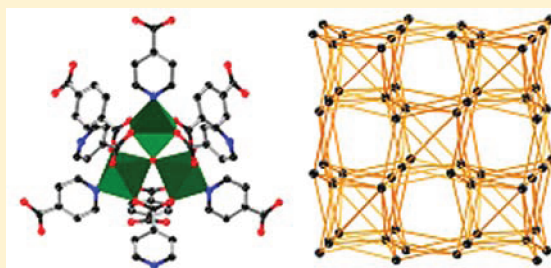


A Nine-Connected Mixed-Ligand Nickel-Organic Framework and Its Gas Sorption Properties

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ABSTRACT: A nine-connected metal–organic framework $[\text{Ni}^{\text{II}}_2\text{Ni}^{\text{III}}(\mu_3\text{-OH})(\text{IN})_3(\text{BDC})_{1.5}] \cdot x\text{Solvent}$ (BDC = benzene-1,4-dicarboxylate, IN = isonicotinate) has been prepared and characterized. The application of the scale-down chemistry through the use of the short and inexpensive BDC and IN ligands leads to a smaller pore size and lower surface area but little compromise in H_2 sorption properties. The compound exhibits a high CO_2 uptake of $73.1 \text{ cm}^3 \text{ g}^{-1}$ (273 K and 1 atm) despite its moderate Langmuir and BET surface areas (888.3 and $571.0 \text{ m}^2 \text{ g}^{-1}$, respectively). Its H_2 uptake (1.47 wt % at 77 K and 1 atm) is also quite high, comparable to that of many materials with high surface area.



Metal–organic frameworks (MOFs) have generated considerable interest due to their intriguing topologies and diverse functionality.^{1,2} The past several decades have witnessed the extensive construction of low-connected networks such as 3-, 4-, and 6-connected topologies. Recently, high-connectivity (>8) MOFs have received increasing attention because of their potential advantage in enhancing the stability of the frameworks for gas adsorptions.³ In comparison with the widely reported low-connected materials, examples of the high-connected MOFs, especially those with simple and uninodal networks, are relatively rare.^{3–5} The difficulty in the construction of the high-connected MOFs results from the restricted coordination numbers of metal centers and steric hindrance of common organic ligands.^{4a} To increase the number of the connections, the utilization of f-block metal ions,⁶ polynuclear metal clusters,^{4b–e,5} and ring and cage aggregates^{4f} as framework nodes has been proposed and demonstrated.

The building block approach is an effective and widely used strategy for the synthesis of MOFs. Among many clusters capable of serving as secondary building unit (SBU) for the construction of frameworks, metal-carboxylate clusters are of particular importance because of the flexible coordination modes and tailorable features of carboxylate ligands.⁷ In most of the reported metal-carboxylate frameworks, besides the metal–carboxylate bonding, metal ions often bind to terminal solvent molecules, leading to the reduced connectivity. Pyridyl carboxylate ligands are often introduced to replace terminal solvent molecules to increase the connectivity.^{3,4e,5d} By the combination of ditopic dicarboxylate and pyridyl carboxylate ligands, Chen and co-workers^{5c} reported a porous coordination polymer (MCF-19) with ncb topology using relatively long ligands. Because gas sorption properties, especially at ambient pressures, do not

necessarily scale with the pore size and because the pore size comparable to the size of gas molecules is often desirable for enhancing host–guest interactions, we have sought to study various approaches to optimize the pore size, for example, through the variation of the pore space by incorporating organic cations of different sizes or through the partition of the pore space upon the formation of the core–shell architecture.^{2d,e,h} Here, we explore the use of scale chemistry by scaling down the size of both ligands used in MCF-19. Advantages of this approach include the likely enhanced thermal stability and lower cost of ligands. Herein we report the construction of $[\text{Ni}^{\text{II}}_2\text{Ni}^{\text{III}}(\mu_3\text{-OH})(\text{IN})_3(\text{BDC})_{1.5}] \cdot x\text{Solvent}$ (Compound 1, Scheme 1), which is the scaled-down version of MCF-19 by using two shorter and inexpensive ligands, benzene-1,4-dicarboxylate (BDC) and isonicotinate (IN). Its gas adsorption properties demonstrate that despite the scaled-down pore size and much lower surface areas compared to MCF-19, there is little change in the H_2 sorption properties.

The solvothermal reaction of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and H_2BDC with HIN in a mixed solvent of DMA and methanol afforded green crystals of compound 1. Single-crystal X-ray diffraction analysis reveals that compound 1 crystallizes in high-symmetry cubic space group $I\bar{4}3m$ with the ncb topology. As shown in Figure 1a, a planar cluster built up with one $\mu_3\text{-OH}$ group and three nickel ions is encapsulated by six carboxyl groups (three from BDC and three from IN) and three pyridyl groups of IN to form a nine-connected SBU. The SBUs are further linked by

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Scheme 1. Synthesis of Compound 1

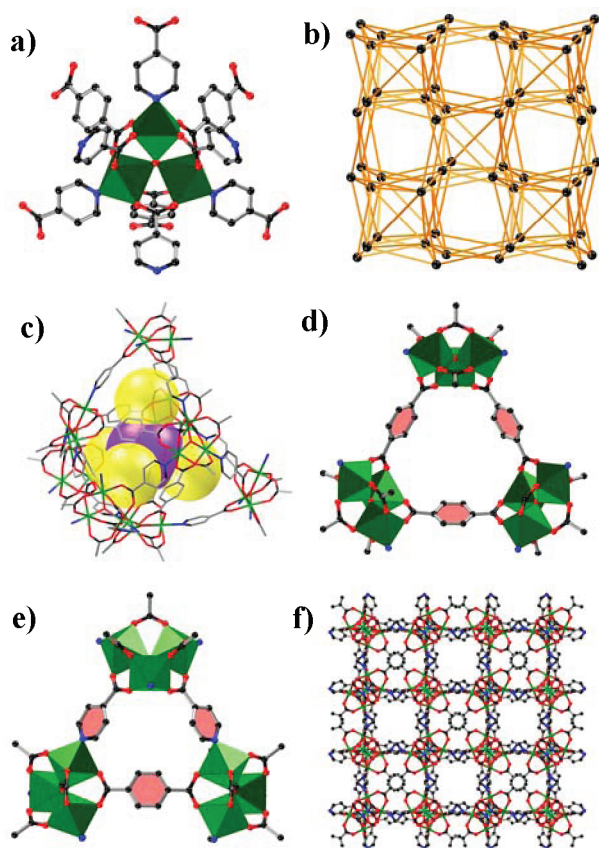
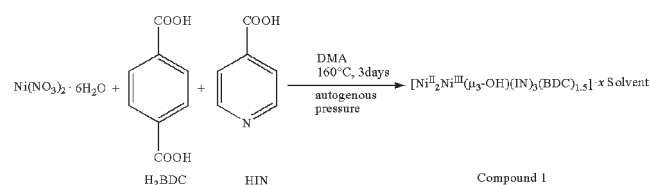


Figure 1. (a) View of the coordination environment of Ni atoms and the trinuclear cluster as node showing nine-connection with six INs and three BDCs in compound 1; (b) an extended ncb network; (c) the cages in the crystal shown as purple and yellow spheres; (d) the linking by BDC between the nodes of the central purple cage; (e) the linking by IN and BDC between the nodes of the peripheral cage; (f) 3-D framework of the crystal, showing the NbO-type channel system.

BDC and IN units to form a uninodal nine-connected network (Figure 1b). Two kinds of cages, the central purple one and the surrounding four yellow ones in the ratio of 1:4 (Figure 1c), are found in the 3D framework. As can be seen from Figure 1d, the central cage is enclosed by four SBUs with six BDC bridging units. The free window diameter of the cage was estimated to be 3.2 Å. For the peripheral four cages, each of them is surrounded by four SBUs, three of which are shared with the central cage. In comparison with only one type of linkage (by BDC) between the nodes of the central cage, there are two types of linkages (BDC and IN) between the nodes of the surrounding cages (Figure 1e). The free window diameters of such cages (2.9 Å) are smaller than those of the central one. Apart from the cages in the framework,

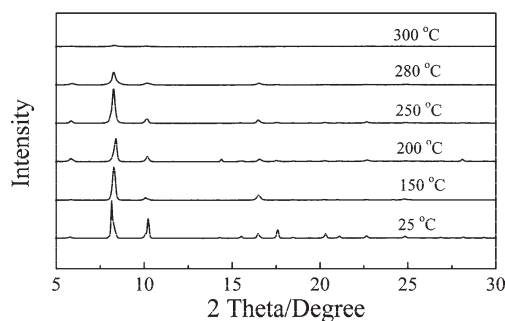


Figure 2. PXRD patterns of the as-synthesized sample heated at different temperatures under N_2 atmosphere.

there exists a NbO-type channel system with the free aperture about 3.4 Å. According to PLATON calculations, the solvent-accessible void of the crystal accounts for 48.1% of the crystal volume.

Thermogravimetric analysis of compound 1 indicates a weight loss in the temperature range 30–65 °C, corresponding to the release of water molecules. From 65 to 270 °C, there is a slight loss of weight, likely due to the removal of a small number of DMA molecules in channels or cages (Figure S1 in the Supporting Information). To determine the thermal stability of compound 1, powder XRD patterns of the sample heated at different temperatures for 1 h under flowing N_2 atmosphere were measured. As can be seen from Figure 2, there is no obvious change in the XRD pattern of the sample heated at temperatures up to 280 °C, indicating that the framework was maintained after the loss of solvent molecules. Compared with the reported stability of MCF-19 at 250 °C,^{5c} the present material exhibits comparable or perhaps improved thermal stability. In consideration of the difference between the frameworks of the two materials, i.e. the replacement of the ligands of naphthalene-2,6-dicarboxylate and 4-(pyridine-4-yl) benzoate in MCF-19 with benzene-1,4-dicarboxylate (BDC) and isonicotinate (IN) in compound 1, it would not be surprising if the shorter ligands contribute to the improved thermal stability of the framework.

To investigate the porosity of the present material, gas adsorption measurements (N_2 , H_2 , CO_2 , and CH_4) were performed on a Micromeritics ASAP 2020 surface area and pore size analyzer. A comparison of sorption data between compound 1 and MCF-19 is given in Table S2 of the Supporting Information. Prior to the measurements, the sample was exchanged with dichloromethane and then degassed at 85 °C under vacuum. As can be seen from Figure 3a, compound 1 exhibits a typical type I adsorption isotherm characteristic of permanent microporosity. The Langmuir and Brunauer–Emmett–Teller (BET) surface areas were calculated to be 888.3 and 571.0 $\text{m}^2 \text{g}^{-1}$, respectively. According to the Horvath–Kawazoe method, the pore size of 5.1 Å and the pore volume of 0.313 $\text{cm}^3 \text{g}^{-1}$ were also calculated.

The hydrogen adsorption study revealed that compound 1 can adsorb 164 $\text{cm}^3 \text{g}^{-1}$ (1.47 wt %) of H_2 at 1.0 atm and 77 K (Figure 3a), which is comparable to that of MCF-19 (1.56%)^{5c} and better than the case of many reported MOFs.⁸ In comparison with MCF-19, the use of the two shorter ligands leads to the decrease in the size of the cages and channels in the present case. However, clearly, there is no significant loss in the hydrogen uptake capacity, which may be due to the enhancement of the interaction with H_2 caused by small pore sizes in our material.⁹ Compound 1 also exhibits a high CO_2 uptake capacity of 73.1 $\text{cm}^3 \text{g}^{-1}$ at 273 K and

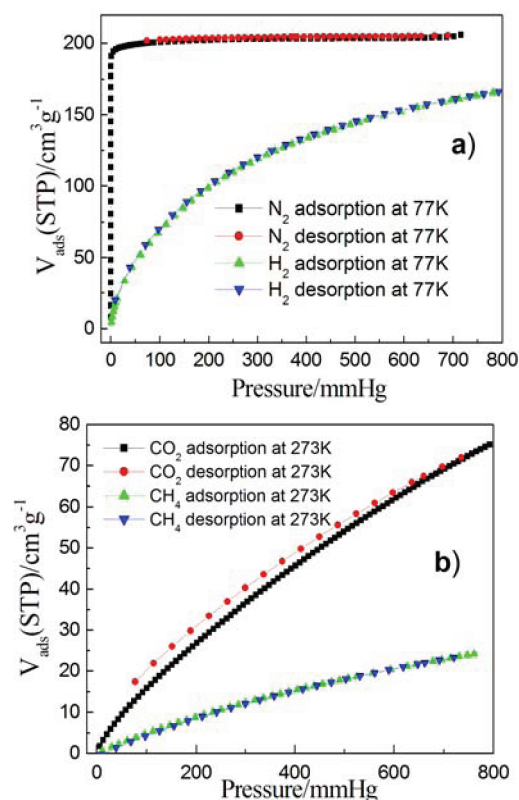


Figure 3. (a) N_2 and H_2 adsorption/desorption isotherms at 77 K; (b) CO_2 and CH_4 adsorption/desorption isotherms at 273 K.

1 atm (Figure 3b). The enthalpy of CO_2 adsorption at the zero loading is around 26.7 kJ/mol, calculated using data measured at 195 K (Figure S5 of the Supporting Information) and 273 K. H_2 and CO_2 adsorption results support that the matching of the pore sizes with the size of gas molecules may be an important factor in designing and synthesizing MOFs for adsorption applications. In addition, in our material, the adsorption of CH_4 gas was markedly lower than that of CO_2 , with an uptake of $24.2 \text{ cm}^3 \text{ g}^{-1}$ at 273 K and 1 atm. Such selective adsorption of CO_2 over CH_4 is of interest for the potential application in the gas separation process.

It is worth noting that the mixed ligand strategy in this work is based on two 180° ditopic ligands with $-2/-1$ charge complementarity. Prior to this work, highly porous MOFs based on ditopic and tritopic ligands with $-3/-2$ charge complementarity (e. g., UMCM-1, UMCM-2, and DUT-6) or two ditopic ligands with complementary bond geometry (e.g., CPM-2 with 120° and 180° ligand bond angles) have been reported.¹⁰ The extraordinary porosity and structural features shown by these materials provide an inspiration for further exploring the mixed carboxylate system. While there has been much focus on the scale-up chemistry, the scale-down chemistry possesses some unique advantages. Such scale-down chemistry, is, however, not without significant challenge, because, in addition to the length of ligands, other factors such as pore-filling by solvent molecules (or counterions in the case of charged frameworks) and possible bond rotations can play dominant roles. For example, more than just in dimension, H_3BTB (1,3,5-tris(4-carboxyphenyl)benzene) is significantly different from H_3BTC (1,3,5-benzenetricarboxylic acid), because its peripheral benzene rings are not coplanar with the central benzene ring, leading to significant

geometrical difference in the metal–carboxyl bonding geometry in BTB-MOFs, compared to that in BTC-MOFs. In the present work, the shortening of the ligands without accompanying rotations of donor sites (oxygen and nitrogen atoms) may play a key role in the success of our synthesis.

In conclusion, a nine-connected cubic porous material has been successfully synthesized by using a mixed-valent trinuclear Ni cluster as uninodes together with simple and low-cost ligands of BDC and IN. The present work provides an interesting example of the scale-down chemistry in the construction of high-connected porous MOFs with no compromise in the H_2 uptake capacity.

■ ASSOCIATED CONTENT

S Supporting Information. Crystal structure information (CIF) and more experimental details and data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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