A twofold interpenetrating polyhedron-based metal–organic framework with high hydrothermal stability was prepared using a rigid and bent C$_2$-symmetric ligand containing two 3,5-benzenedicarboxylate units, which have large surface area and high uptake capacities for various gas molecules.

Metal–organic frameworks (MOFs) are widely studied because of their potential applications in many areas such as gas storage, separation, drug delivery, sensor technology, and catalysis. MOFs have received particular attention as potential hydrogen storage materials. For the practical application of MOFs in the areas of gas storage and/or separation, not only is it their large surface area, suitable pore-size distribution, and exposed metal sites that are important factors to be considered but also their hydrothermal stability.

Among the numerous studies devoted to the preparation of MOFs, it has been found that carboxylates are especially effective in the generation of families of porous materials. In the ongoing search for new ligands based on carboxylates for the construction of stable MOFs with permanent porosity, researchers have become interested in the 3,5-benzenedicarboxylate (bdc) unit because the 120° angle between the two carboxylate groups of the bdc unit could lead to a metal–organic cuboctahedron (MOC) based on the Cu paddle-wheel secondary building unit (SBU), which can provide large inherent pores. The PMOF had a twofold interpenetrating network and catalysis.
topology with a large solvent cavity and potential exposed metal sites at the Cu paddle-wheel SBU of the MOC.

In this study, we designed a new ligand, 1,3-bis(3,5-dicarboxyphénylényl)benzène (H₂L), that contains the same two bdc units but is connected via a bent but rigid linking moiety instead of a flexible linking group. This could lead to a robust and highly stable isoreticular PMOF having interesting gas sorption properties (Figure 1).

When the H₄L ligand was reacted with Cu(NO₃)₂ · 3H₂O in the mixed-solvent dimethylformamide (DMF)/H₂O in the presence of a small amount of HCl under solvothermal conditions, blue block-shaped crystals were obtained (see the Supporting Information, SI). X-ray diffraction (XRD) analysis of the crystal revealed a twofold interpenetrating 3D MOF structure, [Cu₂₂L₁₂(DMF)₈(H₂O)₁₆]·8DMF (I, PMOF-3; Figure 2).

In each net, the bdc units of the ligand are connected to generate the MOCs based on the paddle-wheel-like Cu₂−(COO)₄ SBU (see the top right of Figures 3, S1, and S2 in the SI). The MOCs, having a cavity of ~1.2 nm in diameter, are further interconnected to a 3D structure via four bent but rigid covalent linkages in two different ways. The first type of linkage has a tetragonal cage of type A, consisting of two Cu paddle-wheels and four ligand components (see the middle right of Figure 3, with a cavity of ~0.5 nm in diameter), and the second type of linkage generates a tetragonal cage of type B, consisting of four Cu paddle-wheels and four ligand components (see the bottom right of Figure 3, with a cavity of ~1.3 nm in diameter). Each cuboctahedral cage is connected to six neighboring cuboctahedral cages via four tetragonal prismatic cages of type A and two tetragonal prismatic cages of type B to form a 3D framework of a simple cubic network topology. This arrangement leads to the fourth supertetragonal cage, ~3 nm in size, in the center of eight MOCs in the simple cubic network topology. However, the pore of the fourth cage is almost filled with the MOC belonging to the other interpenetrating net (Figure S3 in the SI).

The cavities of the various cages in PMOF-3 are interconnected to form a 3D cavity through the square windows (~7 Å in diameter) of the MOC. Even though PMOF-3 is the second type of linkage generating a tetragonal cage of type B, consisting of four Cu paddle-wheels and four ligand components (see the bottom right of Figure 3, with a cavity of ~1.3 nm in size, in the center of eight MOCs in the simple cubic network topology). However, the pore of the fourth cage is almost filled with the MOC belonging to the other interpenetrating net (Figure S3 in the SI).

In order to investigate the sorption properties of PMOF-3, gas sorption studies were performed on frameworks 1a and 1b. Both adsorbed significant amounts of N₂ and displayed type I adsorption isotherms, which is typical of a crystalline microporous material (Figure 4a). Sample 1a adsorbs 347 cm³/g of N₂ at 77 K and 1 bar. The Brunauer–Emmett–Teller (BET) and Langmuir surface areas of 1a were 1200 m²/g and 1490 m²/g, respectively. There was a significant increase in the adsorption amount of N₂ in sample 1b of about 470 cm³/g, corresponding to the BET and Langmuir surface areas estimated to be 1840 m²/g and 2020 m²/g, respectively, which are slightly smaller than those of...
When the H$_2$ pressure was increased to 20 bar at 77 K, the excess H$_2$ uptake of 1b reached its maximum, namely, 3.4 wt %, as shown in Figure 4d. This is similar to that of HKUST-1, which has a similar surface area and exposed metal sites. However, at ambient temperature, the H$_2$ uptake of PMOF-3 is still very low, namely, 0.32 wt % at 50 bar, in spite of the presence of the exposed metal sites and the interpenetration of the framework. The isosteric heat of the H$_2$ adsorption of PMOF-3 is still too low, and the pore-size distribution is not optimal for ambient-temperature H$_2$ uptake.

At 195 K and 1 bar, the adsorption amounts of CO$_2$ and CH$_4$ on sample 1b were 725 and 129 g/L, respectively (Figure S7 in the SI). 1b had slightly lower uptake capacities for these gas molecules than those of the best known SNU-5, namely, 862 and 167 g/L, under similar conditions, but had superior selectivity for CO$_2$ over CH$_4$ than SNU-5. Although for 1b the methane adsorption capacity, 148 v/v at 298 K and 50 bar, and the adsorption amount of CO$_2$, 255 v/v at 298 K and 40 bar, were much lower than the best values reported for CH$_4$, PCN-14 (230 v/v, at 290 K and 35 bar), and for CO$_2$, MIL-101c (390 v/v at 304 K and 50 bar), the high hydrothermal stability of PMOF-3 still renders it potentially useful in various gas sorption applications.

In summary, a novel twofold interpenetrating PMOF, [Cu$_{24}$L$_{12}$ (DMF)$_8$ (H$_2$O)$_{16}$]$_3$ 8DMF (PMOF-3), with exposed metal sites could be prepared using a covalently connected MOP-based approach. Despite the interpenetration, the solvent cavity of the PMOF is quite large because of the large inherent cavity of the MOP building blocks. The thermal and hygroscopic stabilities of the PMOF have been demonstrated in VT-PXRD and N$_2$ sorption experiments. In addition, the PMOF has a large surface area and corresponding gas sorption capacities for various gas molecules, including H$_2$. Although the capacities for those gas molecules are not the best, the hydrothermal stability of the framework and the selectivity for some gas molecules might be utilized in various gas sorption applications.

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**Supporting Information Available:** Experimental procedure, crystallographic details and an X-ray crystallographic file in CIF format, XRD patterns, TGA plots, and some graphics. This material is available free of charge via the Internet at http://pubs.acs.org.
