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Isoreticular Metal-Organic Polyhedral Networks Based on 5-Connecting Paddlewheel Motifs

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A metal-organic polyhedral network with a unique 5-connected topology is expanded into a series using different metal ions or dicarboxylate ligands. The prototype material (ZmID), $[Zn_4(mip)_4(dabco)(OH_2)_2]$ (mip = 5-methyl-isophthalate, dabco = diazabicyclo[2.2.2]octane), is based on 5-connecting paddlewheel motifs and possesses large cage-like pores (8−20 Å diameter). The metal ion is replaced by Co^{2+} and/or the dicarboxylate by isophthalate (ip) or 2,7-naphthalenedicarboxylate (2,7-ndc) to give isoreticular frameworks $[Zn_4(ip)_4(dabco)(OH_2)_2]$ (ZID), $[Co_4(ip)_4(dabco)(OH_2)_2]$ (CID), and $[Zn_4(2,7-ndc)_4(dabco)(OH_2)_2]$ (ZND). X-ray powder diffraction and gas sorption studies reveal that ZID and CID have sustainable pore structures and show higher N_2 uptakes than ZmID. ZND is found unstable with respect to the removal of guest solvents. ZmID, ZID, and CID are all similar in terms of the H_2 sorption capacities (1.4−1.5 wt % at 77 K and 1 bar) and isosteric heat of H_2 adsorption (6−7 kJ/mol at low coverage).

Introduction

The possibility of facile and systematic modulation of pore environments is one of the features that make metal-organic frameworks (MOFs) a highly attractive target in application-oriented research for industry,[1] such as gas separation, storage, and others.[2] By varying small components of a network in a systematic manner while keeping the overall topology unchanged, one has a better chance of discovering specific structure−function relationships via effective screening processes. The synthesis of isoreticular frameworks, however, does not appear to be a routine practice in the field of MOF research, and only a limited number of cases are known in literature[3] since Yaghi and co-workers reported a series of frameworks related to $[Zn_4(O)(bdc)_3]$, better known as MOF-5.[4]

One of the topical issues in MOFs is metal-organic polyhedral nets which are characterized by interconnected cage-like pores rather than straight channel-type pores.[5] The differences in the pore structures may result in different behavior in the physisorption of gases. Therefore, the studies on the properties of systematically modulated polyhedral nets in a series are important.

Our group has recently reported that Zn^{2+}, 5-methylisophthalate (mip), and diazabicyclo[2.2.2]octane (dabco) self-assemble to form a unique 5-connected MOF based on three different semi-regular polyhedra.[6] The framework has the formula $[Zn_4(mip)_4(dabco)(OH_2)_2]$ and is abbreviated to

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Scheme 1. Metal Ions and Dicarboxylate Ligands Used to Build a Series of Homologous Frameworks
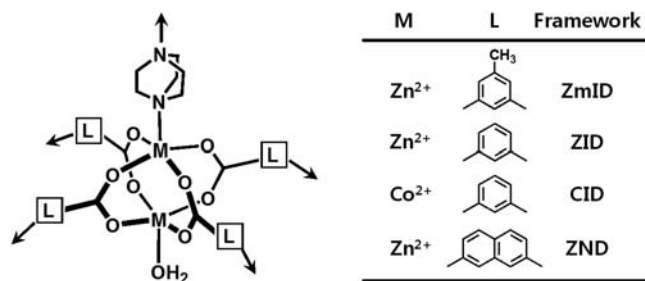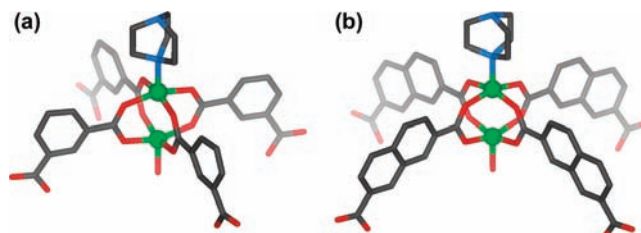

ZmID hereafter. In the present study we elaborated the synthesis to obtain a series of homologous frameworks using different dicarboxylate ligands or metal ions (Scheme 1). The crystal structures and hydrogen sorption properties of the new frameworks are reported here.

Experimental Section

Materials and Methods. $Zn(NO_3)_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, isophthalic acid (ipH_2), and 2,7-naphthalenedicarboxylic acid ($2,7\text{-}ndcH_2$) were obtained from commercial sources. TGA data were obtained on a SCINCO S-1000 instrument, with a heating rate of 5 °C min^{-1} in the air. The TGA data are shown in Supporting Information, Figure S1. The IR spectra were recorded on KBr pellets using a Varian FTS 1000 instrument (Supporting Information, Figure S2–S4). The X-ray powder diffraction (XRPD) patterns were recorded on either a Bruker D8 Advance or a Rigaku RINT2000 system equipped with a Cu sealed tube ($\lambda = 1.54178$ Å).

Synthesis of ZID. $Zn(NO_3)_2 \cdot 6H_2O$ (0.290 g, 0.98 mmol) and $H_2(ip)$ (0.162 g, 0.98 mmol) were dissolved in dimethylformamide (DMF, 15 mL), and the resulting solution was heated to 110 °C for 14 h in a sealed vial. After filtering off a small amount of white precipitate, the filtrate was divided into 5 equal portions. Freshly prepared solutions of dabco (0.044 g, 0.39 mmol) in CH_3CN (2.0 mL) were carefully layered on each of the DMF solution. Shiny crystals deposited within several days; however, they were collected after 5 months to maximize the yield. The product was washed with DMF, guest-exchanged with $CHCl_3$, and dried under vacuum for 12 h. The yield was 0.210 g or 75% based on $Zn_4(ip)_4(dabco)$-$(OH_2)_2(DMF)$. EA Calcd: C, 43.22; H, 3.45; N, 3.69. Found: C, 43.60; H, 3.97; N, 4.37%.

Synthesis of CID. $CoCl_2 \cdot 6H_2O$ (0.106 g, 0.45 mmol) was dissolved in DMF (10.0 mL), and $H_2(ip)$ (0.075 g, 0.45 mmol) and

dabco (0.051 g, 0.45 mmol) were added to it in order. The reaction mixture was homogenized to a dark blue slurry by stirring for about 10 min. After filtering off a powdery precipitate, the filtrate was heated to 92 °C for 60 h in a flame-sealed glass tube. The product formed as dark green-blue crystals. The as-synthesized material was washed with DMF, guest-exchanged with $CHCl_3$, and dried under vacuum for 12 h. The yield was 0.032 g or 26% based on $Co_4(ip)_4(dabco)(OH_2)_3(DMF)_{0.5}$. EA Calcd: C, 43.33; H, 3.45; N, 3.20. Found: C, 42.89; H, 3.76; N, 3.48%.

Synthesis of ZND. A DMF solution (15.0 mL) containing $Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1.0 mmol) and $H_2(2,7\text{-}ndc)$ (0.217 g, 1.0 mmol) was heated to 110 °C for 32 h in a sealed vial. Afterward, the reaction mixture was filtered to remove a small amount of powdery precipitate, and then divided into 5 equal portions. Freshly prepared solutions of dabco (0.034 g, 0.3 mmol) in CH_3CN (1.0 mL) were carefully layered on each of the DMF solutions. Colorless, cut-tetrahedral crystals of varying size formed and were collected after 9 days. The product was washed with DMF, guest-exchanged with $CHCl_3$, and dried under vacuum for 12 h. The yield was 0.210 g or 57% based on $Zn_4(2,7\text{-}ndc)_4(dabco)(OH_2)_2(DMF)_2$. EA Calcd: C, 49.13; H, 4.12; N, 3.82. Found: C, 48.61; H, 3.76; N, 4.11%.

X-ray Crystallography. For ZID and ZND, single crystals were directly picked up from the mother liquor, attached to a glass fiber, and transferred to a cold stream of liquid nitrogen (−100 °C) for data collections. The full hemisphere data were collected on a Siemens SMART CCD diffractometer with Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å). After the data integration (SAINT) and semiempirical absorption correction based on equivalent reflections (SADABS), the structure was solved by direct methods and subsequent difference Fourier techniques (SHEXLTL). Diffractions by the crystals of ZND were very weak probably because of the large fraction of volume occupied by disordered solvents. For CID, single crystals were picked up with a cryoloop attached to a goniometer head, and transferred to a cold stream of liquid nitrogen (−183 °C). The data collection was carried out using synchrotron X-ray ($\lambda = 0.70000$ Å) equipped with ADSC Quantum 210 CCD detector at Pohang Accelerator Laboratory. After the data integration (HKL2000) and space group determination (XPREP), the structure was solved by direct methods and subsequent difference Fourier techniques (SHEXLTL). All the framework atoms were refined anisotropically. After adding hydrogen atoms to their geometrically ideal positions, the diffused electron densities resulting from the residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON,[7] and the results were attached to the CIF file. The coordinated water molecules were left without hydrogen atoms because they could not be located from difference maps. The rotationally disordered dabco ligands and the dynamic

Figure 1. 5-connecting paddlewheel SBUs in ZID (a) and ZND (b). CID is isostructural with ZID and not shown. Hydrogen atoms are omitted.

(5) (a) Tranchemontagne, D. J.; Ni, Z.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 5136–5147. (b) Perry, J. J., IV; Kravtsov, V. Ch.; McManus, G. J.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2007**, *129*, 10076–10077. (c) Dincă, M.; Han, W. S.; Liu, Y.; Dailly, A.; Brown, C. M.; Long, J. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 1419–1422. (d) Ma, S.; Sun, D.; Ambrogio, M.; Fillinger, J. A.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2007**, *129*, 1858–1859. (e) Dincă, M.; Dailly, A.; Brown, C. M.; Neumann, D. A.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 16876–16883. (f) Ma, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 11734–11735. (g) Park, K. S.; Ni, Z.; Côte, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci.* **2006**, *103*, 10186–10191. (h) Huang, X.-C.; Lin, Y.-Y.; Zhang, J.-P.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1557–1559. (i) Lu, W.-G.; Su, C.-Y.; Lu, T.-B.; Jiang, L.; Chen, J.-M. *J. Am. Chem. Soc.* **2006**, *128*, 34–35. (j) Ni, Z.; Yassar, A.; Antoun, T.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 12752–12753. (k) Fang, Q.; Zhu, G.; Xue, M.; Sun, J.; Wei, Y.; Qiu, S.; Xu, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 3845–3848. (l) Alvarez, S. *Dalton Trans.* **2005**, 2209–2233. (m) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. *Science* **2005**, *309*, 2040–2042.
(6) Chun, H. *J. Am. Chem. Soc.* **2008**, *130*, 800–801.

(7) Spek, A. L. *PLATON, a multipurpose crystallographic tool*; Utrecht University: Utrecht, The Netherlands, 2001. SAV is slightly underestimated because of the dynamic disorder of dicarboxylate ligands.

Table 1. Summary of Crystal Data and Structure Refinements

	ZID	CID	ZND
formula	$C_{38}H_{32}N_2O_{18}Zn_4$	$C_{38}H_{32}N_2O_{18}Co_4$	$C_{54}H_{40}N_2O_{18}Zn_4$
FW	1066.14	1040.38	1266.36
T (K)	173(2)	90(2)	173 (2)
λ (Å)	0.71073	0.70000	0.71073
crystal system	Cubic		
space group	$Fm\bar{3}m$		
a (Å)	39.931(4)	39.693(5)	46.627(6)
V (Å^3)	63671(10)	62538(13)	101374(24)
Z	24		
ρ_{calcd} (g/cm^3)	0.667	0.663	0.498
μ (mm^{-1})	0.924	0.657	0.585
$F(000)$	12912	12624	15408
crystal size (mm^3)	$0.60 \times 0.60 \times 0.60$	$0.28 \times 0.25 \times 0.09$	$0.60 \times 0.60 \times 0.40$
reflections collected	77863	106864	82189
independent reflections	2695 ($R_{int} = 0.0641$)	3149 ($R_{int} = 0.1545$)	2634 ($R_{int} = 0.1404$)
T_{max}/T_{min}	0.6070/0.6070	0.9432/0.8374	0.7997/0.7204
data/restraints/parameters	2695/78/103	3149/54/120	2634/18/114
GOF on F^2	1.087	1.131	1.142
R_1, wR_2 [$I > 2\sigma(I)$]	0.0618, 0.1560	0.0702, 0.1695	0.0607, 0.1431
R_1, wR_2 (all data)	0.0713, 0.1636	0.0794, 0.1744	0.0832, 0.1546
largest different peak/hole (e/Å^3)	0.845/−0.627	0.500/−0.503	0.372/−0.624

disorder found in the ip ligands in CID and ZID have been treated with split-atom models. Details of the data collection and structure refinements are summarized in Table 1.

Gas Sorption Studies. The nitrogen sorption isotherms were measured with a custom-built vacuum manifold following a standard volumetric technique at 77 K. The sorption of hydrogen was measured with liquid nitrogen (77 K) or liquid argon (87 K) as the coolant. The gases used were of extra-pure quality (N50 for nitrogen and N60 for hydrogen). In all cases, approximately 0.200 g of crystalline samples were soaked in CHCl$_3$ for 1 d and evacuated under a dynamic vacuum (10^{-3} torr) at room temperature for 12 h. A part of the N$_2$ sorption isotherm in the P/P_0 range 0.05−0.30 was fitted to the Brunauer−Emmett−Teller (BET) equation to estimate the BET surface area. For the Langmuir surface area, data from the whole adsorption isotherm were used. The heat of hydrogen adsorption was calculated using the known method.[8]

Results and Discussion

The standard protocol of solvothermal synthesis used for ZmID has also been applied, with some modifications, to obtain [Zn$_4$(ip)$_4$(dabco)(OH$_2$)$_2$], [Co$_4$(ip)$_4$(dabco)(OH$_2$)$_2$], and [Zn$_4$(2,7-ndc)$_4$(dabco)(OH$_2$)$_2$] which are abbreviated to ZID, CID, and ZND, respectively, hereafter. The reaction conditions described here are carefully optimized so that the products crystallize as phase-pure, single-crystalline materials.

The structures of the 5-connecting paddlewheel units of ZID, CID, and ZND determined by X-ray crystallography are shown in Figure 1.

The three new frameworks are identical with ZmID in terms of the secondary building units (SBUs) and the network topologies. The nets are built upon three different polyhedra which again are built from three different polygons, triangles, squares, and hexagons, with the paddlewheel SBUs at the nodes. Therefore, these materials possess three kinds of cage-like pores (with 8−20 Å diameter) which are interconnected through triangular (3.7 Å) and square (6.6 Å) windows. Note that the hexagonal windows in ZmID are blocked by the methyl groups of mip ligands. ZID and CID which are

isostructural inherit all of these features from ZmID, and additionally the hexagonal windows are open with Y-shaped free passages. The fraction of solvent-accessible voids in ZID and CID is virtually the same, and accounts for at least 67% of the total crystal volume.[7] The 3D net and the Connolly surface of ZID are shown in Figure 2. The latter is an informative representation revealing the size and shape of guest-accessible voids.[9]

ZND is an augmented version of ZID where the dicarboxylate linkage is extended to 11.7 Å from 9.3 Å in ZID (Figure 3). The dabco linkage is not changed at 9.6 Å. The seemingly uneven extension, however, does not disrupt the symmetry and topology of the uninodal 5-connected net. This is because the extended linkers constitute all the edges of the triangle and square motifs, and only the hexagonal motif is composed of alternating dicarboxylate and diamine linkers, preserving the 3-fold rotation symmetry. Meanwhile, we are not sure at the moment whether the uneven lengths of the linkers contribute to the instability of the ZND framework upon evacuation (vide infra). The cage-like pores found in ZND after considering the van der Waals surface are in the range 12−24 Å in diameters. The total solvent-accessible void in ZND accounts for 78% of the crystal volume.

Thermal gravimetric analyses (TGA) show that the decomposition of the frameworks occurs no earlier than 300 °C after a considerable weight loss corresponding to the guest solvents (Supporting Information, Figure S1). However, the true stability of the porous nets has been established by measuring XRPD after evacuating the materials because TGA is insensitive to the collapse of open structures which are not accompanied by a weight change. According to the results of XRPD (Figure 4), which also proves the purity of the bulk phases, ZID and CID show a number of strong peaks at the expected positions, indicating the sustainability of the porous structures shown in Figure 2.

Unlike ZID and CID, however, the diffraction patterns of ZND show very poor profiles when measured after evacuation. Therefore, the augmented framework is not thought

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(9) Connolly, M. L. *J. Appl. Crystallogr.* **1983**, *16*, 548–558.
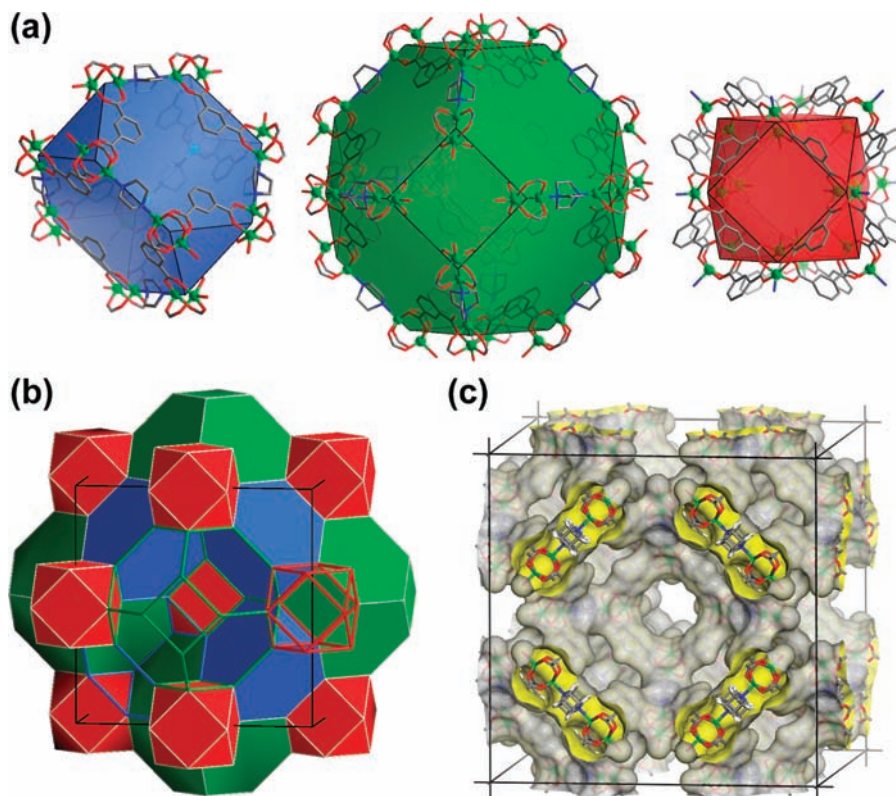
Figure 2. Three different polyhedral cages (a) and the overall packing structure of ZID shown as space-filling polyhedra (b). (c) The Connolly surface of ZID generated with the probe radius of 1.4 Å. Solid lines are the unit cell edges (39.9 Å).
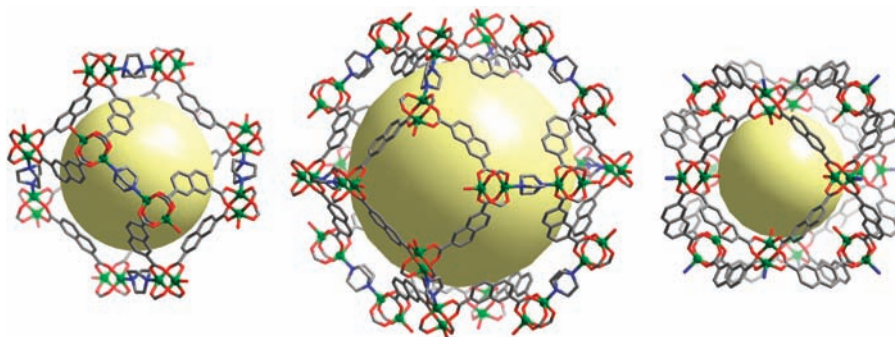
Figure 3. Truncated tetrahedral, truncated octahedral and cuboctahedral cages (from left to right) in ZND. The overall network is similar to Figure 2b. Hydrogen atoms are omitted for clarity.

to be robust with respect to the removal of guest solvents. This has later been confirmed by gas sorption studies in which no meaningful amount of sorption was observed by ZND.

The N_2 sorption isotherms of ZID and CID are compared to those of ZmID in Figure 5. As expected, all the isotherms are similar with typical type I behavior which is characteristic for microporous materials. The total pore volumes of ZID and CID are 0.86 and 0.97 cm³/g, respectively, and these values are 8 and 23% higher than that of ZmID (0.79 cm³/g). By the same token, the Langmuir (BET) surface areas for ZID and CID are higher with 2420 (1609) and 2722 (1802) m²/g, respectively. For comparison, ZmID has the Langmuir (BET) surface area of 2178 (1533) m²/g. The higher values of N_2 uptake by ZID and CID compared to ZmID are because the absence of substituents on the phenyl rings of ip ligands provides additional space for N_2 sorption, and, at the same time, lowers the material density. The total N_2 uptake capacities for isostructural ZID and CID are somewhat different with 26 and 29 N_2 molecules per formula unit, respectively. This difference may be due to the partial loss of coordinated solvent molecules in CID rather than the difference in the formula weight which is 2.5%.

The H_2 sorption has also been measured for ZmID, ZID, and CID at 77 and 87 K, and the isotherms are shown in Figure 6. The data and the corresponding Langmuir—Freundlich fits indicate that the sorption of H_2 is far from being saturated at 77 K and 1 bar. Nevertheless, the differences in the H_2 uptake capacities of the three frameworks at 77 K and 1 bar are not significant with 1.4−1.5 wt % H_2. The values are similar to or somewhat lower than other known MOFs having similar surface areas or similar chemical compositions.[10] The presence of large, cage-like pores may be responsible for the somewhat low H_2 uptakes.

(10) Collins, D. J.; Zhou, H.-C. *J. Mater. Chem.* **2007**, *17*, 3154–3160.
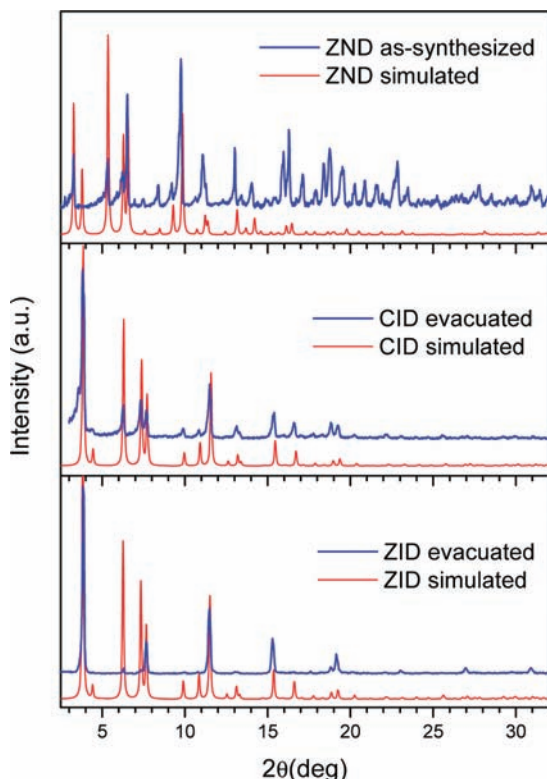
Figure 4. Simulated and experimental X-ray powder diffraction patterns. ZID and CID are measured after guest-exchange with CHCl$_3$ and evacuation for 12 h. ZND is for an as-synthesized sample.
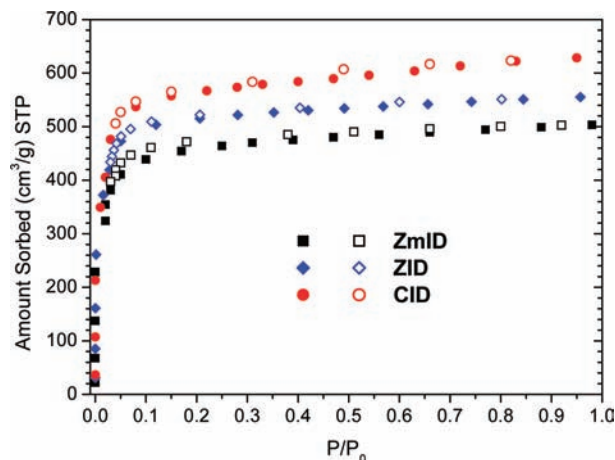
Figure 5. N$_2$ sorption isotherms measured at 77 K. Filled and open symbols denote sorption and desorption, respectively.

The isosteric heat of hydrogen adsorption has been estimated by measuring the H$_2$ sorption at 87 K and following a method known in the literature.[8] According to it, the sorption of H$_2$ on ZID and CID is only slightly more exothermic than on ZmID with the low-coverage values in the range 6−7 kJ/
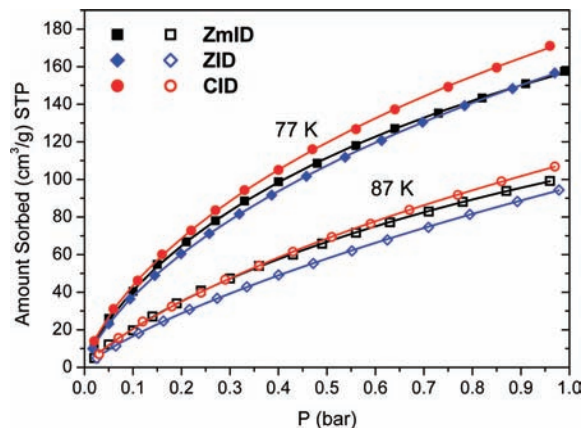
Figure 6. H$_2$ adsorption isotherms measured at 77 and 87 K. Desorption isotherms follow the adsorption branches without a notable hysteresis (not shown). Solid lines are the Langmuir−Freundlich fits.

mol (Supporting Information, Figure S10). Under high-coverage conditions, the heats of H$_2$ adsorption on the three frameworks are similar to each other, and the values converge to about 5 kJ/mol. Again, these values are typical for other known examples in MOFs.[11] These results from H$_2$ sorption studies not only support our belief that straight channels and large open pores are not favored in H$_2$ sorption[12] but also corroborate with the studies on hydrogen desorption in MOFs.[13]

In conclusion, we have shown that the combination of paddlewheel SBUs, angular dicarboxylate, and linear diamine ligands produces polyhedral networks which can readily be expanded into a series. The fact that using linear dicarboxylates instead of angular dicarboxylates in otherwise the same combination results in MOFs with straight-channel type pores[14] is an illustration of the well-known design principles of supramolecular chemistry.[15] The polyhedral networks presented in this work do not possess exceptionally high storage capacities for hydrogen probably because of the spherical cage-like pores with large diameters (1−2 nm). In this regard, further modulation of the pore environments, such as the decoration of pore walls or narrowing down the free passages, may be attempted and should be possible.

Supporting Information Available: The plots of TGA and IR, analysis of gas sorption data and crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Panella, B.; Hönes, K.; Müller, U.; Trukhan, N.; Schubert, M.; Pütter, H.; Hirscher, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 2138–2142.

(14) Chun, H.; Moon, J. *Inorg. Chem.* **2007**, *46*, 4371–4373.

(15) The combination of paddlewheels and terephthalate linkers both of which being "divergent" forms simple channel-type polymers while the use of "convergent" isophthalate results in polyhedral networks with capsular subunits. For details, see, Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: Chichester, England, 2005; p 479.