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Microporous Frameworks

Bottom-Up Synthesis of Porous Coordination Frameworks: Apical Substitution of a Pentanuclear Tetrahedral Precursor[**]

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Coordination compounds with backbones constructed from metal ions that function as connectors, and ligands that function as linkers are generally referred to as coordination polymers.[1,2] This term was first used in the early 1960s, and the field was first reviewed in 1964.[3] Although coordination polymers had been known for many years, it was the seminal work of Robson and co-workers some 18 years ago[4] that made significant initial steps in the synthesis of coordination frameworks. This work explored the building-block methodology that allows the production of certain network topologies based on the selection of metal and ligand geometries. Some time later, the molecular building block (MBB) approach was developed by Wuest[5] and Hosseini,[6] who put forward the strategy of molecular tectonics. This strategy is based on tectons[7] (from tekton, the Greek word for builder), which are special molecules with multiple peripheral sites that have strong directional interaction. Thus, networks with predictable architectures can also be engineered by designing programmed and active molecular tectons. No less important is the concept of secondary building units (SBUs), which was devised by Yaghi and co-workers,[8] and defines the geometry of the units by the points of the extension. SBUs are different from MBBs and do not contain distinct synthetic units that are employed as starting points in the synthesis. Instead, conceptual molecular complexes and cluster entities are formed in situ. These strategies undoubtedly help to shed light on the prediction, design, and synthesis of the resulting. However, in the above approaches, it is not easy to identify metal ions with which the intended framework geometry can be generated, or to establish the exact chemical conditions for the in situ formation of specific SBUs. This uncertainty arises from the existence of various coordination numbers for a given metal. To overcome these difficulties, a new stepwise synthetic approach has been developed,[9] which involves a presynthesized inorganic precursor and a subsequent substitution process that occurs between the precursor and the organic ligand. To realize a step-by-step synthetic scheme for the construction of a target network, three key requirements need be addressed: 1) the selected precursor should remain intact throughout the construction process, 2) the precursor should have an intrinsic geometry as well as specific coordination directionality, in order to guarantee an a priori synthesis of structures, and 3) the precursor should also be soluble in common organic solvents, in order to ensure the feasibility of the subsequent cluster framework formation.

After careful consideration, we chose the metal cluster $[Zn_5(btz)_6(NO_3)_4(H_2O)]$ (**1**, btz = benzotriazolate) as an initial reaction precursor because similar pentanuclear clusters have proven to meet the above criteria.[9b] The pentanuclear cluster has a tetrahedral structure, which has a Zn^{2+} ion at each vertex of the tetrahedron and the fifth Zn^{2+} ion at the center. Each Zn^{2+} ion at the apical positions bears a chelating nitrate group (Figure 1, left). In principle, these coordinated nitrate groups could be fully substituted by linear carboxylate ligands. The tetrahedral geometry of **1** would thus ensure the formation of a four-connected diamondoid (dia) framework (Figure 1).[10] To verify the feasibility of this reaction, the bonding interactions between the benzoate (or nitrate) groups and the central five-core cluster were analyzed by energy decomposition analysis.[11] The calculated results suggest that benzoate groups have larger total bonding energies than nitrate groups (see the Supporting Information). Furthermore, ESI-MS studies conducted with a solution of **1** in *N,N'*-dimethylacetamide (DMA) at 85 °C indicate that the tetrahedral structure of **1** remains stable in solution.

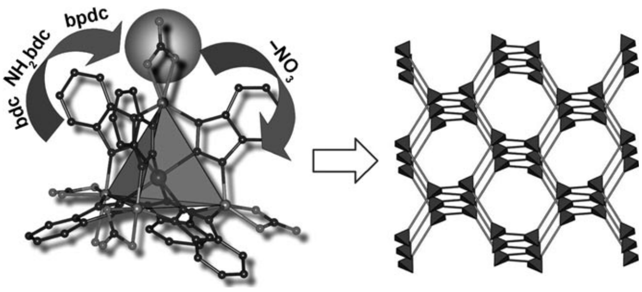

Figure 1. Representation of the substitution of nitrate groups in **1** by linear organic linkers to form extended dia nets.

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Inspired by these results, we present herein a series of linear ditopic carboxylate linkers, namely, 1,4-benzenedicarboxylate (bdc), amino-1,4-benzenedicarboxylate (NH_2bdc), and 4,4′-biphenyldicarboxylate (bpdc; Scheme S1 in the Supporting Information), and the systematic design and construction of three three-dimensional porous coordination polymers $[Zn_5(btz)_6(bdc)_2(H_2O)_2]\cdot 7DMA$ (**2**), $[Zn_5(btz)_6(NH_2bdc)_2(H_2O)_2]\cdot 7DMA$ (**3**), and $[Zn_5(btz)_6(bpdc)_2(H_2O)_2]_{1.5}\cdot 10DMA$ (**4**), which are assembled from **1** and the carboxylate linkers. The formulations of **2**–**4** were supported by microanalysis and thermogravimetric analysis (TGA) results. The phase purity of bulk products was confirmed by X-ray powder diffraction (XRPD).

The precursor **1** was prepared from $Zn(NO_3)_2\cdot 6H_2O$ and 1*H*-benzotriazole (hbtz) in methanolic solution. The solvothermal reaction of the acid forms of bdc, NH_2bdc, or bpdc with **1** in DMA solution afforded complexes **2**, **3**, and **4**, respectively.

Complex **2** crystallizes in the tetragonal space group $I4_1/a$ and, as expected, all the nitrate groups that were bonded to the apical sites of **1** were replaced by bdc linkers. Therefore, from a topological perspective, each pentanuclear cluster corresponds to a tetrahedral node and is linked to four crystallographically equivalent clusters into a typically three-dimensional dia network. The large adamantanoid cages in a single dia net exhibit maximum dimensions of 42.49 × 37.91 × 42.49 Å (Figure S1 in the Supporting Information). The spacious nature of the single network allows three other identical dia networks to penetrate it in a normal mode,[12] thus resulting in a fourfold interpenetrating dia array (Figure 2a and Figure S2 in the Supporting Information). An analysis of the interpenetration topology with the TOPOS program[13] reveals that it belongs to class IIa, that is, the individual nets are related by means of a full interpenetration symmetry element. In this case, the fourfold dia nets are generated by a 4_1 screw axis and the nontranslational degree $Z_n = 4$. Only three examples (CSD refcode: LUMDEC, LUMDIG, QEGGUE)[14] with $Z_n = 4$ have been reported (in almost all cases Z_n is 2), all of which are fourfold dia networks that are generated by a 4_1 screw axis. Therefore, compound **2** is a rare case of class IIa with $Z_n = 4$. Furthermore, despite the interpenetration, the framework of **2** remains open, and contains one-dimensional channels of approximately 7.5 × 9 Å and 8.5 × 11 Å along the [100] and [010] directions (Figure S3 in the Supporting Information) that are occupied by crystallographically unresolved solvent molecules (see the Experimental Section). PLATON[15] analysis showed that the effective free volume of **2** is 46 % of the crystal volume (15 783.8 $Å^3$ out of the 34 227.0 $Å^3$ unit cell volume), this value is comparable to that found in some of the most open zeolites, such as faujasite in which the free space is 45–50 % of the crystal volume. The most fascinating structural feature of the fourfold interpenetrated network is an interlaced, quadruple-stranded braid motif. As illustrated in Figure 2b (left), the tetrahedral clusters are bridged by linear bpd spacers to form an infinite helical chain that runs along the *c* axis with a pitch of 37.908 Å. Four such helical chains from four individual dia nets are divided into two groups; each group is composed of a pair of helices of opposite helicity. It is not possible for pairs of homochiral helices of opposite helicity to form a conventional double helix, and therefore the association between the two independent single-stranded helices of each group can be described as a side-by-side polymeric double helix. This helix is a new structural motif that was only previously observed in an organometallic compound formed by head-to-tail hydrogen bonding interactions.[16] The configuration can easily be visualized when the red helix directly located above the blue helix and the yellow helix is above the green helix (Figure 2b). Quite intriguingly, two groups of side-by-side double helices are interwoven in such a way that the openings generated by one group of helices are alternately penetrated by two helices of the other group. In this case, one group enters from the front and the other from the back (Figure 2b, right), thus resulting in an inextricable quadruple-stranded braid. Its peculiar entangled topology is different from that of triple-stranded molecular braid reported recently,[17] in that the latter essentially has the topology of the Borromean links,[18] that is, if any one component is cut then the other two are free to separate. However, in the present case, the whole assembly can be unraveled into four separate pieces only by removal of a side-by-side double helix (Figure S4 in the Supporting Information). Therefore, the peculiar quadruple-stranded braid motif represents a new mode of one-dimensional association and a real example of an entangled topology, which could appear to be only a mathematical curiosity, is identified.

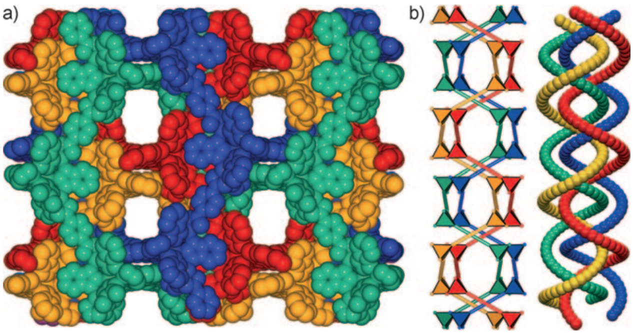

Figure 2. a) A space-filling model of the fourfold interpenetration in **2** viewed down the *a* axis (solvent molecules omitted). b) Views of the interlaced quadruple-stranded braid motif in **2**.

An amine-substituted dicarboxylic acid H_2NH_2bdc was employed as the linking component with the aim of producing additional structures that have the same skeleton as **2** but contain different functionalities. The unit-cell parameters of **3** are very similar to those of **2** and structure determination reveals that the two compounds are isostructural. In **3**, the pentanuclear clusters are assembled through these NH_2bdc linkers, which are somewhat more polar, to generate a fourfold interpenetrating dia framework. Similar to **2**, compound **3** also possesses significant void space that can be accessed from open channels of approximately 9 × 9.5 Å along the *a* axis and 9 × 11 Å along the *b* axis. PLATON analysis showed that the effective free volume of **3** is 44.9 % of the crystal volume (15365.8 Å^3 out of the 34227.0 Å^3 unit cell volume). The smaller free volume of **3** compared to **2** is consistent with the presence of NH_2 groups that decorate the pores in **3**.

The dicarboxylic acid H_2bpdc, which contains biphenyl as a long molecular strut, was employed to further explore the generality of ditopic carboxylate linkers that substitute the nitrate groups, and to investigate the effect of ligand length on the free volume. As anticipated, the structure of **4** is composed of pentanuclear zinc clusters that are joined through long bpdc linkers, and again consists of dia frameworks. The large adamantanoid cages exist in a single dia net and exhibit maximum dimensions of 52.586 × 47.857 × 52.586 Å, which are larger than those in **2** and **3** owing to the larger size of the linker (Figure S5 in Supporting Information). Six such independent networks interpenetrate in the crystal (Figure 3 a), which is consistent with the suggestion of Champness, Schröder, and co-workers that longer ligands lead to a greater degree of interpenetration.[19]

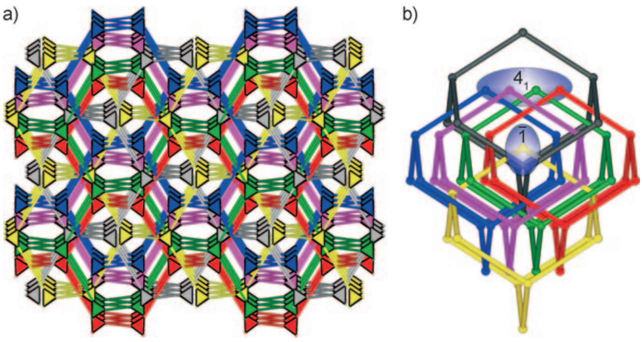

Figure 3. a) A polyhedral presentation of the sixfold interpenetration in **4**. b) Enlarged view of the [4+2] interpenetration mode.

Rather intriguingly, an investigation of interpenetration using the TOPOS program package[13] indicated that the interpenetration mode presented in **4** differs from the normal mode in **2** and **3** and can be described as two sets of normal interpenetrating nets (Figure 3 b and Figure S6 in the Supporting Information). One set (class IIa), which is identical to **2** and **3**, is a fourfold dia network generated by a 4_1 screw axis, and the other (class IIa) is a twofold dia network that is generated by an inversion center. Because the two sets are not related by any symmetry operation but have the same topology, we therefore refer to the current system as a nonequivalent [4 + 2] interpenetrated dia system (Class IIa + IIa)., Blatov, Proserpio, and co-workers have used TOPOS to systematically analyze and rationalize the classes of interpenetration (equivalent,[20] nonequivalent,[21] and hetero-interpenetrating nets[21]) for all the interpenetrating nets in the Cambridge Structural Database (CSD) and Inorganic Crystal Structure Database (ICSD). The results obtained show that there are only a total of 15 nonequivalent cases[22] (2.1 %) among the 301 valence-bonded interpenetrating metal–organic frameworks,[20] 198 interpenetrating inorganic networks,[21] 122 interpenetrated hydrogen-bonded organic networks,[23] and 135 interpenetrated hydrogen-bonded metal–organic systems.[24] Of these, a sixfold interpenetrating three-connected ths ($ThSi_2$) network (CDS ref. code: ZABQIC) also exhibits a non-equivalent [4 + 2] interpenetrated array. Strikingly, even after sixfold interpenetration, the effective free volume of **4** reached 66.4 % of the crystal volume (43914.1 Å^3 out of the 66170 Å^3 unit cell volume, Figure S7 in the Supporting Information), which is greater than the volumes of most open zeolites and comparable to that of previously reported highly porous interpenetrating Pt_3O_4 net (67 %).[25]

To examine the thermal stability and microporosity of these porous networks, **2** was selected for carrying out TGA, XRPD, and N_2 adsorption measurements. The TG curve of **2** reveals a weight loss of 33.4 % from 20 °C to 410 °C, which corresponds to the removal of dma guest molecules and coordinated water molecules (calculated 33.5 %, Figure S8 in Supporting Information). A sample of **2** was soaked in CH_2Cl_2 overnight and then evacuated at 150 °C for 24 h to give the fully desolvated form **2a**, the formation of which was confirmed as no weight loss was observed from 20 to 410 °C (Figure S8 in Supporting Information). XRPD patterns of **2** at 150 °C in a vacuum and 400 °C at standard pressure show sharp diffraction peaks, which indicates the architectural stability of the evacuated framework (Figure 4, inset). Interestingly, when powdered **2a** was soaked in DMA at 70 °C for three days, high-quality single crystals of **2** were obtained, as demonstrated by the coincidence of crystal data. The N_2 sorption isotherm of **2a** at 77 K reveals type I behavior characteristic of a microporous material (Figure 4). The Langmuir surface area was calculated to be 1164 m^2 g^{-1} (BET, 850 m^2 g^{-1}), which is greater than the highest value for classical zeolites, (904 m^2 g^{-1} for zeolite Y),[26] and comparable to those of many porous coordination polymers[27] and mesoporous silica materials (BET, 500–1160 m^2 g^{-1}).[28] The maximum N_2 uptake of 266 cm^3 g^{-1} (at standard temperature and pressure, STP) was reached at 1 atm. The nitrogen adsorption hysteresis can be attributed to the dynamic feature of the framework.

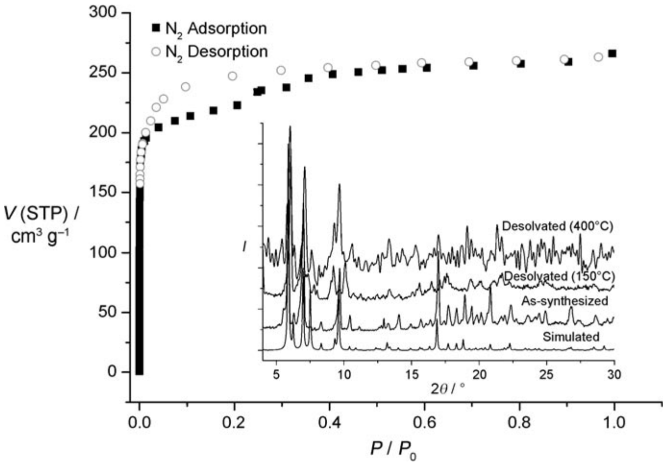

Figure 4. Gas sorption isotherms of **2** for N_2 at 77 K. The inset shows XRPD patterns for as-synthesized and desolvated **2**.

In conclusion, we successfully produced three microporous interpenetrated frameworks by using a predesigned tetrahedral metal cluster and linear organic ligands. Our initial N_2 adsorption results provide an insight into the potential of these porous materials in inclusion chemistry. Similar porous solids based on this pentanuclear cluster with various transition metals have been synthesized and will be subsequently reported.

Experimental Section

1: A solution of $Zn(NO_3)_2 \cdot 6H_2O$ (89 mg, 0.3 mmol) and hbtz (48 mg, 0.4 mmol) in methanol/DMA (1:1, 5 mL) was heated at 100°C for 2 days in a Teflon-lined steel bomb. The resulting colorless crystals were collected, washed with Et_2O, and dried at room temperature (yield: 46 mg, 60% based on Zn). Elemental analysis (%) calcd for **1**: C 33.27, H 1.86, N 23.71; found: C 33.35, H 1.79, N 23.69.

2–**4**: A solution of **1** (65 mg, 0.05 mmol), H_2bdc, H_2NH_2bdc, or H_2bpc (0.3 mmol) in DMA (5 mL) was heated at 85°C for 2 days in a Teflon-lined steel bomb. The resulting colorless octahedral crystals were collected, washed with Et_2O, and dried at room temperature (yield: 70% (**2**), 45% (**3**), and 60% (**4**) based on Zn).

Crystal data for **1**: $C_{36}H_{26}N_{22}O_{13}Zn_5$, $M_r = 1301.77$, monoclinic, space group $P2_1/n$, $a = 10.736$ (5) Å, $b = 15.688(5)$ Å, $c = 29.199(5)$ Å, $\beta = 95.906$ (5)°, $V = 4892(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.765\,\mathrm{mg\,m^{-3}}$, final $R1 = 0.0744$ and $wR2 = 0.1644$ ($R_{int} = 0.0958$) for 8610 independent reflections [$I > 2\sigma(I)$]. **2**: $C_{80}H_{99}N_{25}O_{17}Zn_5$, $M_r = 2009.69$, tetrahedral, space group $I4_1/a$, $a = b = 30.048$ (5) Å, $c = 37.908(5)$ Å, $V = 34226(9)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.560\,\mathrm{mg\,m^{-3}}$, final $R1 = 0.0467$ and $wR2 = 0.0959$ ($R_{int} = 0.0772$ after SQUEEZE) for 15230 independent reflections [$I > 2\sigma(I)$]. **3**: $C_{80}H_{101}N_{27}O_{17}Zn_5$, $M_r = 2039.73$, tetrahedral, space group $I4_1/a$, $a = b = 30.048$ (5) Å, $c = 37.908(5)$ Å, $V = 34226(9)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.583\,\mathrm{mg\,m^{-3}}$, final $R1 = 0.0595$ and $wR2 = 0.1086$ ($R_{int} = 0.1662$ after SQUEEZE) for 14918 independent reflections [$I > 2\sigma(I)$]. **4**: $C_{136}H_{154}N_{37}O_{24}Zn_{7.5}$, $M_r = 3181.24$, tetrahedral, space group $I4_1/a$, $a = b = 36.211$ (2) Å, $c = 50.989(2)$ Å, $V = 66858(5)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.264\,\mathrm{mg\,m^{-3}}$, final $R1 = 0.0863$ and $wR2 = 0.1999$ ($R_{int} = 0.0870$ after SQUEEZE) for 19400 independent reflections [$I > 2\sigma(I)$].

Data were collected on a Bruker Apex CCD diffractometer at 298(2) K for **1** to **3** and 150(2) K for **4**, with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares methods with SHELXL.[29] The DMA molecules were highly disordered and could not be modeled properly, thus the SQUEEZE routine of PLATON was applied to remove the contributions to the scattering from the solvent molecules. The reported refinements are of the guest-free structures using the *.hkp files produced using the SQUEEZE routine.

CCDC 715123 (**1**), 715124 (**2**), 715125 (**3**), and 715126 (**4**) contain 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. The Supporting Information includes additional views of the crystal structures, XRPD patterns, and TGA profiles.

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