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Novel One-Dimensional Tubelike and Two-Dimensional Polycatenated Metal–Organic Frameworks

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Two novel metal–organic frameworks (MOFs) [Zn(TITMB)(OAc)](OH)·8.5H_2O (**1**) and [Ag(TITMB)N_3]·H_2O (**2**) [TITMB = 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene, OAc = acetate anion] were synthesized and their structures were determined by X-ray crystallography. Complex **1** crystallizes in tetragonal space group $P\bar{4}$ with a = 23.2664(7) and c = 11.9890(3) Å and Z = 8. **1** has a one-dimensional tubelike structure with large inner pore size of ∼17 Å. Complex **2** crystallizes in monoclinic space group $C2$ with a = 20.7193(10), b = 11.5677(8), and c = 12.2944(6) Å, β = 125.5770(10)°, and Z = 4. **2** consists of two-dimensional honeycomb networks that interpenetrate each other to generate a polycatenated structure. In these two complexes, both zinc(II) and silver(I) atoms are four-coordinated with the same tetrahedral coordination geometry. The topologies of **1** and **2** are predominated by the conformations of TITMB, which are cis, trans, trans in **1** and cis, cis, cis in **2**, respectively.

Introduction

The construction of metal−organic frameworks (MOFs) with novel structures and topologies has attracted great interest from chemists in the past decade because of their potential applications in many fields such as material science, medicine, and chemical technology.[1] From the reported studies, tripodal ligands with an arene core have been found to be one of the most useful organic building blocks in construction of MOFs. For example, metallocages or capsules, infinite one-dimensional (1D) chain, two-dimensional (2D) honeycomb networks, and three-dimensional (3D) architectures have been obtained by assembly reactions of tripodal ligands with transition metal salts.[2−4] The results demonstrated that the formation of MOFs strongly depends on the nature of organic ligands and metal ions as well as counteranions. Especially in the case of flexible tripodal ligands such as 1,3,5-tris(4-pyridylmethyl)benzene,[5] 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene,[6] and 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (TITMB),[7,8] in which the coordinating pyridyl, pyrazol, or imidazole groups were connected to the central aromatic ring through the methylene groups, a variety of MOFs can be expected since such flexible ligands can adopt different conformations according to the different geometric requirements of metal atoms. The TITMB ligand has cis, cis, cis and cis, trans, trans conformations (Chart 1) as observed in the cagelike complexes $[Ag_3(TITMB)_2]X_3$ ($X = ClO_4^-, BF_4^-, NO_3^-$)[7] and 2D network complex $[(dien)_3Cu_3(TITMB)_2](ClO_4)_6$ (dien = diethylenetriamine),[8] respectively. Extending this approach, we now have constructed 1D tubelike complex [Zn(TITMB)-

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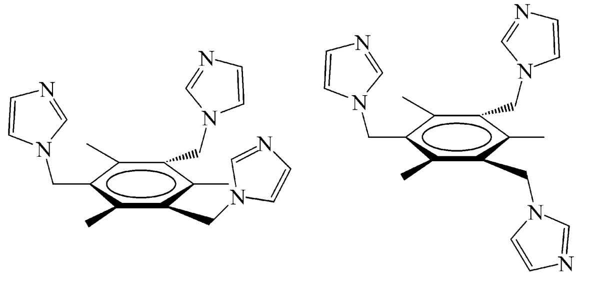
Chart 1



cis,cis,cis *cis,trans,trans*

Table 1. Crystal Data and Refinement Results for Complexes **1** and **2**

param	1	2
chem formula	$C_{23}H_{45}N_6O_{11.5}Zn$	$C_{21}H_{26}AgN_9O$
fw	655.02	528.38
space group	$P\bar{4}$ (No. 81)	$C2$ (No. 5)
a, Å	23.2664(7)	20.7193(10)
b, Å		11.5677(8)
c, Å	11.9890(3)	12.2944(6)
β, deg		125.5770(10)
V, Å^3	6490.0(3)	2396.6(2)
Z	8	4
T, K	93	200
λ, Å	0.7107	0.7107
D_{calcd}, g cm^{-3}	1.341	1.464
μ(Mo Kα), cm^{-1}	8.19	8.72
R1 [$I > 2\sigma(I)$][a]	0. 0635	0.0447
wR2 [$I > 2\sigma(I)$][b]	0. 1303	0.1219

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **1** and **2**

Compound **1**			
Zn1−O71	1.975(5)	Zn1−N12	2.009(5)
Zn1−N302	2.012(5)	Zn1−N502	2.012(5)
Zn2−O73	1.952(4)	Zn2−N52	2.004(5)
Zn2−N102	2.020(5)	Zn2−N32	2.030(5)
O71−Zn1−N12	104.0(2)	O71−Zn1−N302	116.0(2)
O71−Zn1−N502	114.5(2)	N12−Zn1−N302	100.9(2)
N12−Zn1−N502	110.4(2)	N502−Zn1−N302	109.8(2)
O73−Zn2−N52	114.5(2)	O73−Zn2−N102	107.9(2)
O73−Zn2−N32	117.3(2)	N102−Zn2−N52	107.4(2)
N32−Zn2−N52	110.0(2)	N102−Zn2−N32	97.9(2)
Compound **2**[a]			
Ag1−N1	2.293(5)	Ag1−N52$^{\#1}$	2.300(4)
Ag1−N32$^{\#2}$	2.329(4)	Ag1−N12	2.341(4)
N1−Ag1−N52$^{\#1}$	121.08(19)	N1−Ag1−N32$^{\#2}$	109.8(2)
N52$^{\#1}$−Ag1−N32$^{\#2}$	105.99(15)	N1−Ag1−N12	112.8(2)
N52−Ag1−N12$^{\#1}$	100.89(16)	N32−Ag1−N12$^{\#2}$	104.84(17)

[a] Symmetry transformations used to generate equivalent atoms: #1, $x - 0.5$, $y - 0.5$, $z - 1$; #2, x, y, $z - 1$.

(OAc)](OH)·8.5H_2O (**1**) (OAc = acetate anion) and 2D polycatenated honeycomb network [Ag(TITMB)N_3]·H_2O (**2**) by assembly reactions of TITMB with zinc(II) acetate dihydrate and [Ag(NH_3)$_2N_3$], respectively. Here we report the self-assembly and X-ray crystal structures of the novel MOFs. It is interesting that the TITMB has a cis, trans, trans conformation in **1** while the conformation of TITMB in **2** is cis, cis, cis.

Experimental Section

Materials and Measurements. All commercially available chemicals are of reagent grade and used as received without further purification. TITMB was synthesized as reported previously.[8] Ag(NH_3)$_2N_3$ was prepared in situ by addition of diluted ammonia solution to silver azide, which was obtained by the reaction of silver nitrate and sodium azide, until the silver azide was dissolved. Solvents were purified by standard methods prior to use. Elemental analyses of C, H, and N were taken on a Perkin-Elmer 240C elemental analyzer, at the Center of Materials Analysis, Nanjing University. Electrospray mass spectral (ES-MS) measurements were carried out on an LCQ System (Finnigan MAT) using methanol as the mobile phase. Thermogravimetric analysis was performed on a simultaneous SDT 2960 thermal analyzer under flowing N_2 with a heating rate of 10 °C/min. The 500 MHz ^{1}H NMR spectra were measured on a Bruker DRX-500 NMR spectrometer at room temperature.

Preparation of the Complexes. [Zn(TITMB)(OAc)](OH)·8.5H$_2$O (1). In a typical synthesis, an ethanolic solution (40 mL) of zinc(II) acetate dihydrate (110 mg, 0.5 mmol) was added slowly to a solution of TITMB (180 mg, 0.5 mmol) in ethanol (20 mL) and the mixture was stirred for 5 h at room temperature to give a colorless powder with ca. 30% yield. Single crystals suitable for X-ray analysis were obtained by recrystallization from aqueous solution. Anal. Calcd for $C_{23}H_{45}N_6O_{11.5}Zn$: C, 42.18; H, 6.92; N, 12.83. Found: C, 42.14; H, 7.08; N, 12.65.

[Ag(TITMB)N$_3$]·H$_2$O (2). A solution of TITMB (18.0 mg, 0.05 mmol) in acetonitrile (5 mL) was carefully layered over an aqueous solution of freshly prepared Ag(NH_3)$_2N_3$ (0.05 mmol). Colorless crystals were isolated by filtration after several weeks. Yield: 47%. Anal. Calcd for $C_{21}H_{26}AgN_9O$: C, 47.74; H, 4.96; N, 23.86. Found: C, 47.97; H, 5.03; N, 23.51.

Caution! *Azide salts of metal complexes are toxic and potentially explosive and should be handled with care*.

Crystallographic Analyses. A crystal of **1** with approximate dimensions 0.45 × 0.30 × 0.30 mm was mounted, and data collection was carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer at 93 K, using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The intensity data for **2** were collected on the same machine at 200 K. The structures were solved by direct methods using SIR92[9] and expanded using Fourier techniques.[10] All data were refined anisotropically by the full-matrix least-squares method for non-hydrogen atoms. In complex **2**, atoms N2 and N3 in the azide anion disordered into two positions with the site occupancy factors (sof) of 0.577(8) and 0.423(8), respectively. The hydrogen atoms except for those of water molecules were generated geometrically. All calculations were carried out on an SGI workstation using the teXsan crystallographic software package.[11] The crystal parameter, data collection, and refinement results for compounds **1** and **2** are summarized in Table 1. Selected bond length and angles are listed in Table 2. Further details are provided in the Supporting Information.

Results and Discussion

X-ray crystallographic analysis revealed that each zinc(II) atom in **1** is coordinated by three N atoms of imidazole

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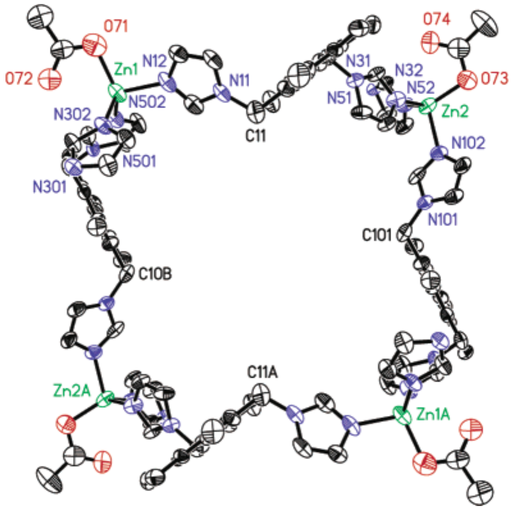

Figure 1. A 48-membered macrocyclic ring for complex **1**. The thermal ellipsoids were drawn at the 50% probability level.

from three different TITMB ligands and one O atom of acetate anion to complete its tetrahedral coordination environment. As a result of such coordination mode, the [Zn(ImCH$_2$R)$_3$(OAc)] (where Im = imidazol-1-yl, R = aromatic ring) unit has a positive charge. A hydroxide anion is present as a counteranion for the charge balance. The presence of hydroxide anion was confirmed by electrospray mass spectral (ES-MS) spectrometry. Prominent peaks of [(TITMB)$_2$Zn$_2$(OAc)(OH)]$^{2+}$ and [(TITMB)$_3$Zn$_2$(OAc)(OH)(H$_2$O)]$^{2+}$ were observed with reasonable isotopic distribution in aqueous solutions of **1**.[12] Four zinc(II) atoms and four TITMB ligands (each TITMB using two of the three pendant arms connects two zinc atoms) form a 48-membered macrocyclic ring through Zn−N coordination bonds (Figure 1). The key point for the formation of such a macrocyclic ring is the cis, trans, trans conformation of TITMB ligand in **1**, while TITMB with cis, cis, cis conformation formed individual cages [Ag$_3$(TITMB)$_2$]X$_3$ (X = ClO$_4^-$, BF$_4^-$, NO$_3^-$) or a 2D honeycomb network [Cu$_3$(TITMB)$_2$(OAc)$_6$]·H$_2$O (**3**) assemblied with the corresponding transition metal salts.[7]

The macrocyclic rings are connected still by Zn−N coordination bonds to give an infinite 1D tubelike chain (Figure 2) with large inner channel. The intermetallic separations of Zn1−Zn2 and Zn1−Zn2A are 13.725(1) Å and 13.595(1) Å [diagonal distances of Zn1−Zn1A and Zn2−Zn2A: 16.380(2) and 18.309(2) Å, respectively], and the distances of C101−C10B and C11−C11A are 11.80(1) and 10.51(2) Å, respectively (atom numbering scheme shown in Figure 1). A previously reported silver(I) coordination polymer containing nanometer-sized tubes was obtained by reaction of 2,4,6-tris[(4-pyridyl)methylsulfanyl]-1,3,5-triazine with silver(I) salts.[3]

There is only one acetate anion as an ancillary ligand coordinated with the zinc(II) atom in **1**. However, in the reported cagelike architectures with tripodal ligands and four-coordinated metal atoms, e.g. [Zn$_3$(TIB)$_2$(OAc)$_6$] (**4**) [TIB = 1,3,5-tris(imidazol-1-ylmethyl)benzene][13] and [(en)$_3$Pd$_3$L$_2$](NO$_3$)$_6$ [en = ethylenediamine, L = 1,3,5-tris(4-pyridylmethyl)benzene],[5] two coordination sites of each metal atom were occupied by two acetate anions or by one ethylenediamine as ancillary ligands. Furthermore, it is noteworthy that TITMB and TIB react with the same zinc(II) acetate dihydrate to form two entirely different MOFs **1** and **4**; the structural difference between TITMB and TIB is just that there are three methyl groups at the 2,4,6-positions of the central benzene ring of TITMB. Reactions of TITMB and TIB with copper(II) acetate also give different MOFs with 2D honeycomb and 3D porous structures.[7b,14] The results imply that even subtle changes of a ligand may have great influence on the formation of MOFs. The steric hindrance of methyl groups in TITMB and the differences in solubilities between TITMB and TIB may contribute to the formation of the 1D chain structure of **1** rather than an individual cage. Three methyl substituents make the TITMB ligand and its zinc(II) complex **1** have lower solubility than TIB and **4** in common solvents such as ethanol, acetonitrile, water, etc. The discrete compound must be unfavorable because of the additional methyl groups of the TITMB preventing the entropically favored [Zn$_3$(TITMB)$_2$]$^{6+}$ structure.

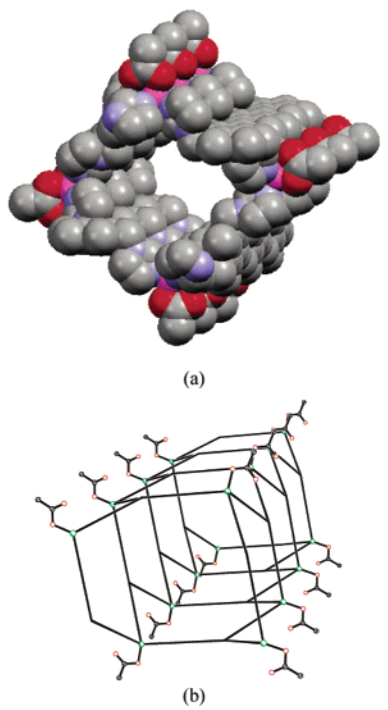

Figure 2. (a) 1D tubelike structure of **1**. (b) Schematic drawing of the tubelike structure of **1** in which the TITMB ligands are simplified by straight lines from the centroid of the central benzene ring to the coordinated zinc atom and water molecules are omitted for clarity.

Complex **1** contains a lot of water molecules (8.5 H$_2$O/zinc atom, most of which are inside the channel; see Figure S1) as revealed by the crystal structure determined at low

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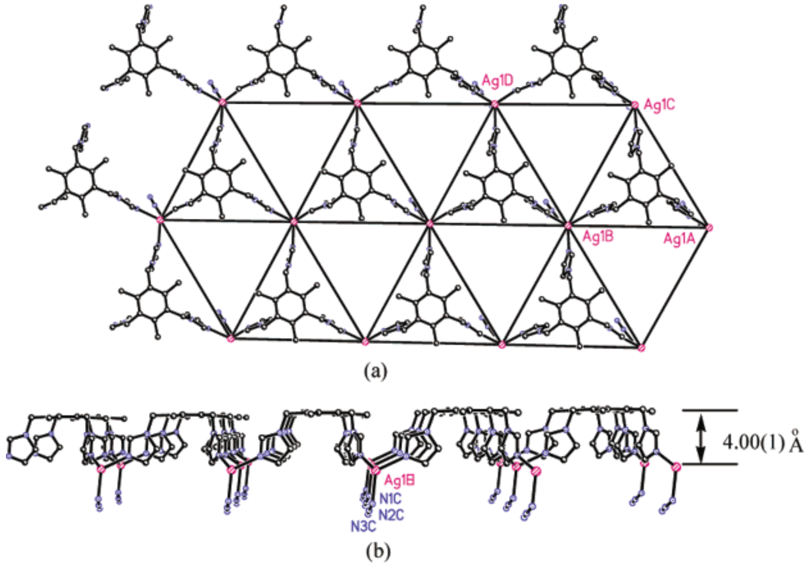

Figure 3. Top view (a) and side view (b) of the 2D network of **2**. Water molecules are omitted for clarity.

temperature (93 K). Distances of C−O and O−O ranging from 2.18(7) to 3.599(8) Å indicate the formation of C−H---O(water), (water)O−H---O(water), and (water)O−H---O(acetate) hydrogen bonds, although most of the hydrogen atoms of the water molecules could not be found. TGA data for **1** exhibited a weight loss of 18.0% (calcd 17.9%) from 25 to 110 °C, representing the loss of uncoordinated water molecules (6.5 H_2O), and no further weight loss was observed until 260 °C. Unfortunately the tubelike structure collapsed after removing the water molecules. The tubelike structure of **1** is expected to have affinity for guest inclusion, which was studied by ^{1}H NMR in D_2O. Upfield shifts of 0.15−0.2 ppm were observed for the methyl and methylene signals of 1-dodecanol when it was added to the D_2O solution of **1** as a guest. The results indicate that **1** may have a capacity for inclusion of an alkyl chain.

To further investigate the assembly of TITMB with transition metal salts, we carried out the reaction of TITMB with $Ag(NH_3)_2N_3$. A complex with the same structure and topology as **1** can be expected if the silver(I) takes a four-coordinated tetrahedral geometry. In this case the coordinated acetate anion in **1** will be replaced by an azide anion and the complex is neutral with one silver(I) and one azide anion. In fact, the crystallographic analysis of **2** indicates that the silver(I) atom is indeed four-coordinated with the same tetrahedral geometry as that of zinc(II) in **1** and the azide anion coordinated to the silver(I) atom as a monodentate ligand as that of acetate anion in **1**. However, the conformations of the TITMB ligand in complexes **1** and **2** are different. In complex **2** the conformation of TITMB is cis, cis, cis while TITMB in **1** has cis, trans, trans conformation. Namely the topologies of MOFs **1** and **2** are predominated by the conformations of the organic ligand. Each TITMB acts as an exo-tridentate ligand and connects three silver(I) atoms to form an infinite 2D honeycomb network in complex **2** as illustrated in Figure 3a. The silver(I) atoms are located in the same layer which was separated from benzene ring plane with a distance of 4.00(1) Å, and the azide anions act as

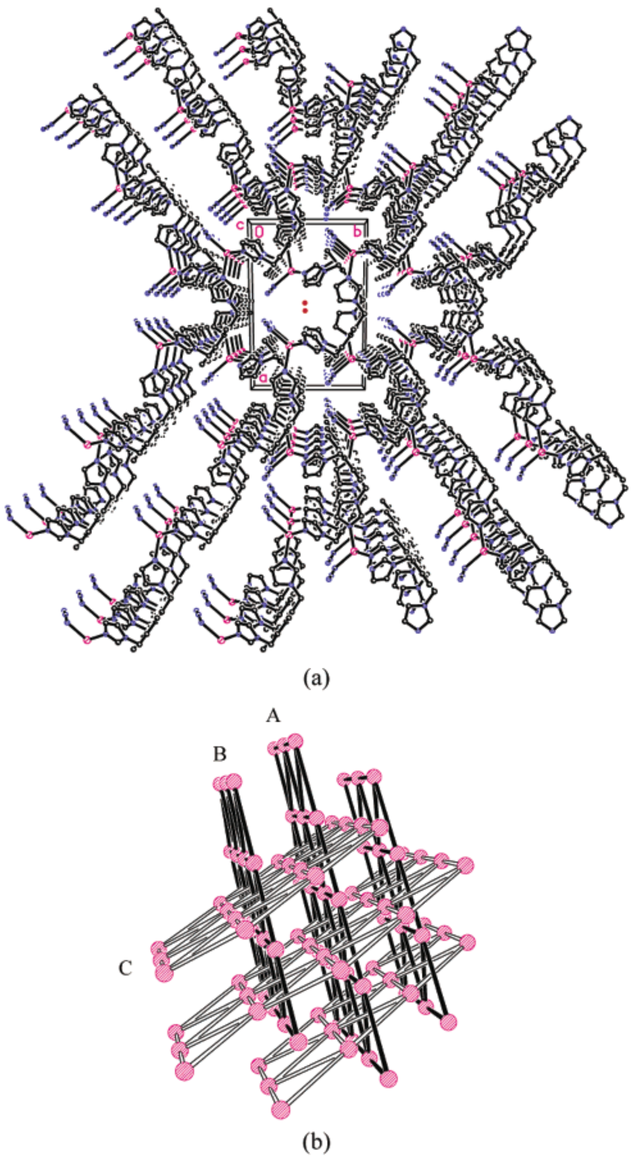

Figure 4. (a) Crystal packing diagram of **2** along the *c* axis. (b) Schematic drawing of the polycatenated framework of **2**.

appending groups from the side view of the network as shown in Figure 3b. In the reported 2D honeycomb network $[Cu_3(TITMB)_2(OAc)_6]\cdot H_2O$ (**3**), the distance between two planes formed by the copper(II) atoms and by benzene rings is 5.00(1) Å,[7] while, in the case of $[Ag(TCB)(CF_3SO_3)]$ (**5**) (TCB = 1,3,5-tricyanobenzene), the silver(I) atoms are trigonally coordinated to three nitriles and fall into the benzene ring plane since the TCB is a tripodal planar ligand.[15]

In the 2D network of complex **2**, three silver(I) atoms form triangles which are "filled" with TITMB ligand (e.g. Ag1A, Ag1B, and Ag1C) and "empty" (e.g. Ag1B, Ag1C, and Ag1D) alternatively as exhibited in Figure 3a. The edge lengths of the triangles, i.e., the intermetallic distance between two silver(I) atoms in Figure 3a, are 11.865(1) (Ag1B−Ag1C), 11.989(1) (Ag1B−Ag1A), and 12.294(1) (Ag1B−Ag1D) Å, respectively. The crystal packing diagram of complex **2** is shown in Figure 4a. The remarkable structural feature of this complex is that the "empty" triangle is large enough to allow the inclusion of another 2D sheet generating a polycatenated network structure (Figure 4b). The dihedral angle between two polycatenated sheets, for example sheets A and C in Figure 4b, is 68.9° implying an inclined interpenetration. Two parallel sheets A and B are separated by a distance of 9.537(1) Å.

In conclusion, a 1D tubelike or 2D honeycomb structure can be formed on the basis of the conformation of the flexible TITMB ligand. The results of present and previous studies show that TITMB is a versatile ligand that can provide MOFs with specific topologies as well as interesting properties.[7,8,16] The large inner pore size (∼17 Å) of the tubelike structure of **1** creates a localized chemical microenvironment in which a compound may have properties different from that of the bulk phase.[17] Further studies, such as chemistry inside the tubelike structure and functionalization of MOFs, are now in progress in our laboratory.

Acknowledgment. The authors are grateful to the National Natural Science Foundation of China for financial support of this work.

Supporting Information Available: Figure S1, showing the tubelike structure of **1** with water molecules inside and outside of the channel, and X-ray crystallographic files, in CIF format. This material is available free of charge via Internet at http://pubs.acs.org.

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