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Molecular Ladders with Multiple Interpenetration of the Lateral Arms into the Squares of Adjacent Ladders Observed for $[M_2(4,4'\text{-bpy})_3(H_2O)_2(phba)_2](NO_3)_2\cdot 4H_2O$ (M = Cu^{2+} or Co^{2+}; 4,4′-bpy = 4,4′-Bipyridine; phba = 4-Hydroxybenzoate)

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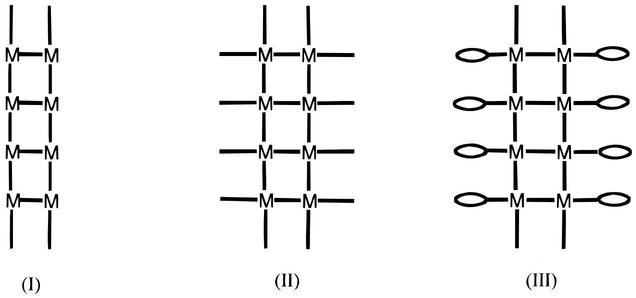
Introduction

The research in metal-directed supramolecular complexes has been rapidly expending because of their fascinating structural diversity and potential applications as functional materials.[1−3] The current topical areas focus on the construction of supramolecular frameworks of novel topology through metal-based coordination and on the crystal engineering of molecular architectures organized by coordinate covalent or supramolecular contacts (such as hydrogen bonding, $\pi-\pi$ interactions, etc.). So far, a wide range of infinite one-, two-, and three-dimensional coordination frameworks, including helicates,[4] diamondoid,[3b,5] honeycomb,[5a,6] square or rectangular grid,[7] T-shaped,[3c,8] ladder,[9] brick wall,[7a,9a] molecular bilayers,[10] octahedral,[11] and other uncommon frameworks,[1d,12] have already been generated with simple, linear *N,N*′-donor spacers such as 4,4′-bipyridine (4,4′-bpy), pyrazine, and related species. In the realm of molecular ladders, most of the molecular ladders have only inner rungs (part I of Chart 1)[9a−i] and two exceptions comprising the same inner rungs and lateral arms have recently documented (part II of Chart 1).[9o,p] To the best of our knowledge, no molecular ladder having different inner rungs and lateral arms has been reported before this work (part III of Chart 1).

Chart 1. Possible Structural Types of Molecular Ladders (I) Having Only Inner Rungs, (II) Having the Same Inner Rungs and Lateral Arms, and (III) Having Different Inner Rungs and Lateral Arms



We have recently reported a series of noninterpenetrating open frameworks with variable cavities or channels in which the rodlike rigid spacers such as 4,4′-bpy, pyrazine, and the related species are chosen as building blocks.[13] We report herein the preparation, crystal structures, and thermal properties of two isomorphous 3-D molecular networks with 1-D channels self-assembled by a new type of molecular ladders having different inner rungs and lateral arms, namely, $[M_2(4,4'\text{-bpy})_3(H_2O)_2$-

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Table 1. Crystallographic and Experimental Data for **1** and **2**

	1	**2**
formula	$C_{44}H_{46}N_8O_{18}Cu_2$	$C_{44}H_{46}N_8O_{18}Co_2$
fw	1101.97	1092.75
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	11.023(3)	11.104(1)
b (Å)	15.398(8)	15.490(1)
c (Å)	14.315(8)	14.390(1)
β (deg)	106.02(2)	106.02(2)
V (Å^3)	2335(2)	2379.0(3)
Z	2	2
ρ_{calc} (g cm^{-3})	1.567	1.525
T (°C)	22	22
λ (Mo Kα) (Å)	0.710 73	0.710 73
μ (Mo Kα) (cm^{-1})	0.997	0.782
R_1 ($I > 2\sigma(I)$)[a]	0.045	0.0443
wR2 (all data)[a]	0.1209	0.1160

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o)^2 + (0.1(\max(0,F_o^2) + 2F_c^2)/3)^2]^{-1}$.

(phba)$_2$](NO$_3$)$_2$·4H$_2$O (M = Cu^{2+} (**1**) and Co^{2+} (**2**), phba = 4-hydroxybenzoate).

Experimental Section

All reagents were commercially available and used as received. The C, H, N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000−400 cm^{-1} on a Nicolet 5DX spectrometer. Thermogravimetric data were collected on a Perkin-Elmer TGS-2 analyzer at a heating rate of 10 °C/min.

Synthesis of [Cu$_2$(4,4′-bpy)$_3$(H$_2$O)$_2$(phba)$_2$](NO$_3$)$_2$·4H$_2$O (1). To a solution of Cu(NO$_3$)$_2$·3H$_2$O (0.242 g, 1.0 mmol) in 4:1 (v/v) MeOH/H$_2$O (10 cm^3), a solution of 4,4′-bpy (0.156 g, 1.0 mmol) in MeOH (5 cm^3) was slowly added with stirring for 20 min at 60 °C, and then a solution of phba (0.138 g, 1.0 mmol) in MeOH (5 cm^3) was slowly added. The solution was adjusted to pH ≈ 4.5 by addition of dilute NaOH solution. Deep-blue block crystals were deposited within 2 weeks in ca. 75% yield based on 4,4′-bpy. Anal. Calcd for $C_{44}H_{46}N_8O_{18}Cu_2$: C, 47.96; H, 4.21; N, 10.17. Found: C, 47.78; H, 4.12; N, 10.00. IR data (cm^{-1}): 3382m, 3100m, 3050m, 2919m, 2850m, 1611vs, 1549s, 1510m, 1492m, 1418s, 1381vs, 1314s, 1223s, 1167m, 1072m, 1044w, 1015w, 859m, 813m, 786m, 728w, 701w, 641m, 576w, 531w, 503w.

Synthesis of [Co$_2$(4,4′-bpy)$_3$(H$_2$O)$_2$(phba)$_2$](NO$_3$)$_2$·4H$_2$O (**2**). It was prepared as for **1** using Co(NO$_3$)$_2$·6H$_2$O in place of Cu(NO$_3$)$_2$·3H$_2$O. Dark-red block crystals of **2** were isolated in ca. 58% yield based on 4,4′-bpy. Anal. Calcd for $C_{44}H_{46}N_8O_{18}Co_2$: C, 47.96; H, 4.21; N, 10.17. Found: C, 47.78; H, 4.12; N, 10.00). IR data (cm^{-1}): 3388m, 3051m, 2918m, 2852m, 1609vs, 1546s, 1510m, 1412s, 1384vs, 1285s, 1229s, 1166m, 1110w, 1068m, 1046w, 1018w, 864m, 814m, 786m, 723w, 702w, 639m, 568w, 533w, 498w.

X-ray Crystallography. Diffraction intensities for the two complexes were collected at 21 °C on a Siemens R3m diffractometer using the ω-scan technique. Lorentz polarization and absorption corrections were applied.[14] The structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs, respectively.[15,16] Non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically (C−H = 0.96 Å); the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[17] The crystallographic data for **1** and **2** are listed in Table 1. Selected bond lengths (Å) and bond angles (deg) for **1** and **2** are given in Table 2. Drawings were produced with SHELXTL.[18]

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1** and **2**[a]

	complex **1**	complex **2**
M(1)−O(1)	1.992(2)	2.001(3)
M(1)−O(2)	2.466(3)	2.480(3)
M(1)−N(1)	2.009(2)	2.020(3)
M(1)−N(2a)	2.001(2)	2.012(3)
M(1)−N(3)	2.041(3)	2.041(3)
M(1)−O(1w)	2.272(2)	2.285(3)
O(1)−C(16)	1.279(4)	1.294(5)
O(2)−C(16)	1.240(4)	1.251(5)
O(1)···O(2w)	2.788(3)	2.810(4)
O(2)···O(3w)	2.731(4)	2.740(4)
O(3)···O(5c)	2.881(6)	2.900(7)
O(1w)···O(2we)	2.694(3)	2.710(4)
O(1w)···O(3wf)	2.763(4)	2.773(4)
O(3w)···O(5g)	2.908(5)	2.916(6)
O(2w)···O(4)	2.836(4)	2.849(5)

	complex **1**	complex **2**
O(1)−M(1)−N(2a)	87.96(9)	88.08(12)
O(1)−M(1)−N(1)	88.33(9)	88.17(12)
N(2a)−M(1)−N(1)	176.17(10)	176.15(14)
O(1)−M(1)−N(3)	163.73(10)	163.98(14)
N(2a)−M(1)−N(3)	87.84(10)	87.73(13)
N(1)−M(1)−N(3)	95.48(10)	95.65(13)
O(1)−M(1)−O(1w)	99.36(9)	99.40(11)
N(2a)−M(1)−O(1w)	96.03(9)	95.92(13)
N(1)−M(1)−O(1w)	85.50(9)	85.54(12)
N(3)−M(1)−O(1w)	96.71(10)	96.42(13)
O(1)−M(1)−O(2)	57.52(8)	57.79(11)
N(2a)−M(1)−O(2)	89.65(9)	89.85(12)
N(1)−M(1)−O(2)	87.58(9)	87.42(12)
N(3)−M(1)−O(2)	106.74(9)	106.73(13)
O(1w)−M(1)−O(2)	156.08(8)	156.36(10)
C(1)−N(1)−M(1)	124.4(2)	124.4(3)
C(5)−N(1)−M(1)	118.12(19)	118.8(2)
C(6)−N(2)−M(1)	121.8(2)	122.3(3)
C(10)−N(2)−M(1)	120.8(2)	120.5(3)
C(11)−N(3)−M(1)	120.7(2)	121.4(3)
C(15)−N(3)−M(1)	121.9(2)	121.5(3)
C(16)−O(1)−M(1)	101.37(18)	101.2(3)
C(16)−O(2)−M(1)	80.47(19)	80.5(3)
O(2)−C(16)−O(1)	120.3(3)	120.2(4)
M(1)−O(1w)···O(2we)	124.92(11)	124.69(13)
M(1)−O(1w)···O(3wf)	112.05(11)	112.28(14)
O(2we)···O(1w)···O(3wf)	102.01(12)	102.10(14)
O(2)···O(3w)···O(5g)	80.69(13)	80.97(15)
M(1)−O(2)···O(3w)	116.87(11)	117.06(13)
O(1)···O(2w)···O(4)	120.56(13)	120.25(15)
N(4)−O(4)···O(2w)	116.6(3)	116.8(4)
C(16)−O(1)···O(2w)	140.22(19)	140.0(3)
M(1)−O(1)···O(2w)	117.90(11)	118.25(14)
C(16)−O(2)···O(3w)	158.9(2)	158.4(3)
C(20)−O(3)···O(5c)	108.5(3)	109.0(3)

[a] Symmetry codes: (a) $x - 1, y, z$; (b) $x + 1, y, z$; (c) $x, -y - {}^1/_2, z + {}^1/_2$; (d) $-x, -y + 1, -z$; (e) $-x, -y, -z$; (f) $x, -y + {}^1/_2, z - {}^1/_2$; (g) $-x + 1, y + {}^1/_2, -z + {}^1/_2$ for **1** and **2**.

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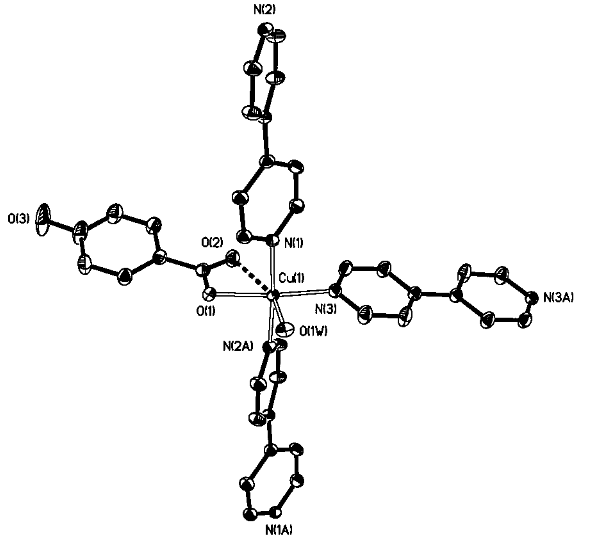

Figure 1. ORTEP view (at 30% probability) of the coordination environment of the metal atom in **1**.

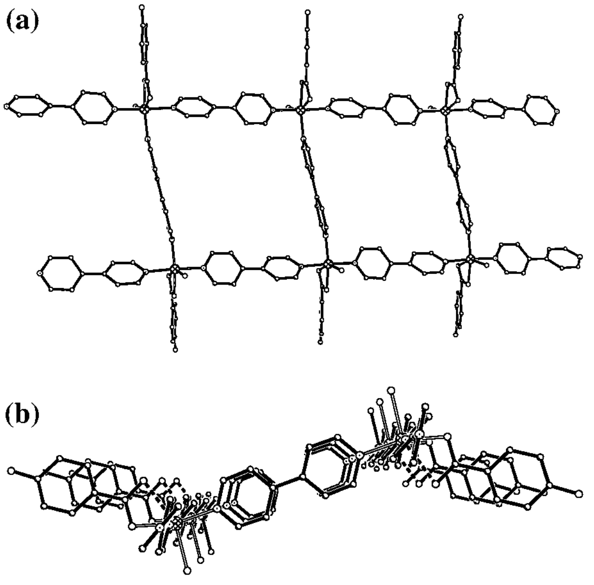

Figure 2. Top (a) and side (b) views showing the cationic 1-D ladder in **1**.

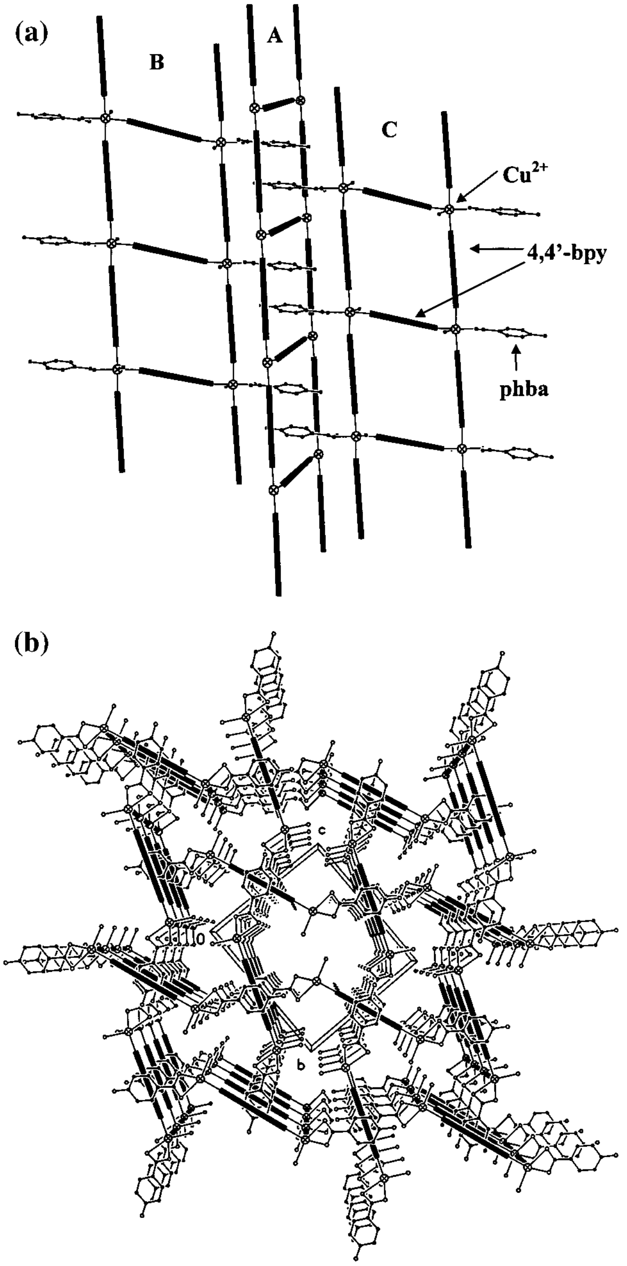

Figure 3. (a) Perspective view showing the threading of lateral arms of two adjacent ladders (B and C) into the squares of a ladder (A), where the 4,4′-bpy ligands are represented as bold lines. The lateral arms (phba ligand) and the aqua ligands of ladder A are omitted for clarity. (b) The 3-D network of **1** viewed from the *a*-axis direction. The 4,4′-bpy molecular rods are also shown as bold lines for clarity.

Results and Discussion

Crystal Structures. Complexes **1** and **2** are isomorphous. **1** is made up of cationic one-dimensional molecular ladders, nitrate ions, and lattice water molecules. An ORTEP view of the coordination environment of the metal atom is depicted in Figure 1. Each Cu(II) atom has Jahn−Teller distorted octahedral coordination geometry, being coordinated by three nitrogen atoms from three different 4,4′-bpy ligands [Cu−N = 2.001(2)−2.041(3) Å], two oxygen atoms from an unsymmetrically chelating carboxylate group of a phba ligand [Cu(1)−O(1) = 1.992(2), Cu(1)−O(2) = 2.446(3) Å], and an aqua ligand [Cu(1)−O(1w) = 2.272(2) Å] where the carboxy O(1) atom and the three nitrogen atoms are located at the equatorial positions and the carboxy O(2) and the aqua ligand are at the axial positions.

Every two 4,4′-bpy ligands and one η^2-phba ligand form a T-shaped geometry at each metal(II) atom [N−M(1)−N = 87.84(10), 95.48(10), 176.17(10)° for **1** and 87.73(13), 95.65(13), 176.15(14)° for **2**]. These T-shaped units are linked to each other through the μ_2-4,4′-bpy bridges to furnish an infinite molecular ladder. The adjacent metal···metal distances along the side pieces and the inner rungs are 11.023, 11.116 Å for **1** and 11.114, 11.182 Å for **2**.

The most common ladder motif has been revealed in most of the reported molecular ladders such as [Cd_2{1,4-bis(4-pyridyl)methylbenzene}$_3(NO_3)_4$],[9a,b] [Co_2(4,4′-bpy)$_3(NO_3)_4$],[9c] [Co_2{1,2-bis(4-pyridyl)ethane}$_3(NO_3)_4$],[9d] [Ag_2(pyrazine)$_3$-$(CF_3SO_3)_2$],[9e] [Cu_2{1,4-bis(4-pyridyl)butadiene}$_3(MeCN)_2$]-$(PF_6)_2$,[9f] [Co_2{1,2-bis(4-pyridyl)ethylene}$_3(NO_3)_4$]·$6CHCl_3$,[9g] [Cd_2{3,6-bis(3-pyridyl)-1,2,4,5-tetrazine}$_3(NO_3)_4$],[9h] and [M_2-{1,2-bis(4-pyridyl)ethyne}$_3(NO_3)_4$] (M = Zn and Co).[9i] Another ladder motif has also been observed in [Co(4,4′-bpy)(μ_2-O_2-$CMe)_2$],[9j] [Cu{1,2-bis(4-pyridyl)ethyne}$(NO_3)_2$]·0.5EtOH,[9k] [Ag-

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{3,6-di(4-pyridyl)-1,2,4,5-tetrazine}]X (X = BF_4^- and PF_6^-),[9l] [Ag{3,6-bis(3-pyridyl)-1,2,4,5-tetrazine}](CF_3SO_3),[9m] [Ag(4,4′-bpy)(μ_2-O_2CMe)]·$3H_2O$,[9n] and [Ag(4,4′-bpy)](H_2PO_4)·H_3PO_4.[9n] The above-mentioned molecular ladder motifs only have inner rungs.[9a−n] Until recently, the ladder motif having inner rungs and lateral arms has been found in [Ni_2(4,4′-bpy)$_5$(H_2O)$_4$](ClO_4)$_4$·3(4,4′-bpy)·$4H_2O$[9o] and [Ag_2(1,2-bis(4-pyridyl)ethyne)$_5$](BF_4)$_2$.[9p] However, the ladder motif revealed in **1** and **2** is unprecedented. As shown in Figure 2, both sides of the ladder in **1** or **2** are occupied by lateral phba ligands. Therefore, these two compounds represent a new ladder motif having different inner (μ_2-4,4′-bpy) rungs and lateral (η^2-phba) arms.

The most interesting feature is the overall three-dimensional molecular network in **1** or **2**. The lateral arms of each molecular ladder are threaded into the [M_4(4,4′-bpy)$_4$] squares of adjacent molecular ladders with each square penetrated oppositely by two phba lateral arms that belong to two different molecular ladders, as shown in Figure 3a. Such multiple threading[9o] results in a novel three-dimensional molecular network with one-dimensional channels running along the *a*-axis direction (Figure 3b). The channels are occupied by the nitrate and water molecule guests that are hydrogen-bonded to each other (O(2w)···O(4) = 2.836(4), O(3w)···O(5g) = 2.908(5) Å) and to the aqua ligand and the carboxy and phenol groups of the phba moieties (O(1w)···O(2we) = 2.694(3), O(1w)···O(3wf) = 2.763(4), O(1)···O(2w) = 2.788(3), O(2)···O(3w) = 2.731(4), O(3)···O(5c) = 2.881(6) Å). The aromatic rings of phba penetrated into the same square are parallel to each other, and the face-to-face separations are about 3.49 Å, indicating significant $\pi-\pi$ interactions.[19] On the other hand, there are significant $\pi-\pi$ interactions between the aromatic rings of phba and those of 4,4′-bpy, with the face-to-face distances in the range 3.36−3.59 Å, resulting in coplanarity of the two pyridyl rings of a 4,4′-bpy ligand. Such an arrangement of the molecular ladders in **1** and **2** is different from that of the ladder in [Ni_2(4,4′-bpy)$_5$(H_2O)$_4$](ClO_4)$_4$·3(4,4′-bpy)·$4H_2O$, in which the lateral arms of the adjacent molecular ladders extend the one-dimensional ladder into a porous sheet structure by $\pi-\pi$ interaction (3.78 Å),[9o] and is also different from that of the ladder in [Ag_2(1,2-bis(4-pyridyl)ethyne)$_5$](BF_4)$_2$, in which the ladder planes are stacked parallel at a distance of 3.51 Å. Each square is therefore penetrated by four lateral arms, two entering by one side and two by the opposite one, thus resulting in another type of supramolecular entanglement.[9p]

Thermal Properties. The thermogravimetric analysis (TGA) data, recorded at 30−650 °C in air, show that **1** first lost weight corresponding to two aqua ligands and four lattice water molecules per empirical formula (obsd, 9.8%; calcd, 9.6%) from 70 to 153 °C. This fact indicates that each aqua ligand is weakly coordinated, in accord with the crystal structure that it is located at the axial position of the elongated octahedron.[13i] Above 200 °C **1** began to decompose gradually. Up to 650 °C, the final residue was analyzed for CuO (obsd, 85.1%; calcd, 85.6%).

On the basis of the thermal decomposition behavior of **1** and those of the related metal−4,4′-bpy coordination polymers,[7c,20] it may be suggested that the lattice water molecules or other solvent molecules can be removed from the cavities of the networks under appropriate thermal conditions while the skeleton of networks is retained and may be used as microporous solids for molecular adsorption, ion exchange, and heterogeneous catalysis.[1−3]

Conclusions

Two isomorphous molecular ladders assembled by different metal salts and 4,4′-bpy have been prepared and characterized. The ladder motif having different inner rungs and lateral arms in **1** and **2** constitutes a novel member of infinite molecular ladders. The lateral arms of each molecular ladder are threaded into the [M_4(4,4′-bpy)$_4$] squares of adjacent molecular ladders; each square is oppositely penetrated by two lateral arms that belong to different molecular ladders. Such multiple threading results in a novel three-dimensional molecular network with one-dimensional channels running along *a*-axis direction.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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