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A novel two-fold interpenetrating 3D $4^2.8^4$ network self-assembled from a new 1D coordination polymer

Jack Y. Lu,*[a] Wifredo A. Fernandez,[a] Zhenghua Ge[a] and Khalil A. Abboud[b]

[a] *Department of Chemistry, University of Houston-Clear Lake, Houston, TX 77058, USA. E-mail: lu@cl.uh.edu*
[b] *Department of Chemistry, University of Florida, Gainesville, FL 32611, USA*

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A new metastable coordination polymer, $[Cu(4,4'\text{-bipy})(NO_3)_2]_n$ (4,4′-bipy = 4,4′-bipyridine, **1**), has been synthesized. Its subsequent reactions with additional 4,4′-bipy resulted in a self-assembled metal-organic framework, $\{[Cu(4,4'\text{-bipy})_2(H_2O)_2][Cu(4,4'\text{-bipy})_2(H_2O)(NO_3)]\}(NO_3)_3 \cdot 12H_2O$ (**2**), featuring two-fold interpenetrating 3D $4^2.8^4$ networks.

Introduction

It is well-known that active metal centers play a very important role in catalysis, molecular recognition, and the functionality of metal-organic framework (MOF) coordination polymers.[1] Extensive research efforts have been devoted worldwide to the utilization of such metal centers in catalytic processes in chemical reactions. One of the difficulties for achieving such metal centers has been the stabilization and structural characterization of these species with active open metal (OM) sites.[2] Single crystal structures are mostly derived from stable phases that rely on a good crystallization of the compound to give single crystals of suitable quality for X-ray diffraction analysis. The as-synthesized compounds with OM sites, however, are metastable. The isolation of single crystals of such metastable species with OM sites is rare due to the inherent difficulty to stabilize the structure at the metastable stage of crystallization. Although a recent paper reported on the generation of OM sites by thermal removal of the labile coordinating water molecules from the as-synthesized structure,[2b] further utilization of OM-site-containing coordination polymers has been hardly reported. Herein, we present a new metastable one-dimensional (1D) coordination polymer with active OM sites, $[Cu(4,4'\text{-bipy})(NO_3)_2]$ (4,4′-bipy = 4, 4′-bipyridine), **1**, and the construction of a novel three-dimensional (3D) MOF, $[Cu(4,4'\text{-bipy})_2(H_2O)_2][Cu(4,4'\text{-bipy})_2(H_2O)(NO_3)]][NO_3]_3 \cdot 12H_2O$, **2**, from the 1D coordination polymer **1** by utilizing its active OM sites.

Experimental

Synthesis

$[Cu(4,4'\text{-bipy})(NO_3)_2]$ (4,4′-bipy = 4, 4′-bipyridine),1. $Cu(NO_3)_2 \cdot 2.5H_2O$ was reacted with 4,4′-bipy (4,4′-bipy = 4, 4′-bipyridine) in a mole ratio of either 1 : 1 or 1 : 2 in the presence of iodine under hydrothermal conditions, in a 23 ml acid digestion bomb, at 120 °C for 3 days. Both reaction ratios produced purple crystals of complex **1**. The crystals were isolated and dried in air and were suitable for single crystal X-ray diffraction analysis. Subsequent reactions attempted in the absence of iodine were not successful in producing complex **1** under the given conditions.

$[Cu(4,4'\text{-bipy})_2(H_2O)_2][Cu(4,4'\text{-bipy})_2(H_2O)(NO_3)]][NO_3]_3 \cdot 12H_2O$, 2. Crystals of complex **1** were allowed to stand in the original solution in the presence of excess 4,4′-bipy overnight. The labile nitrates and the open metal sites from **1** were replaced by additional 4,4′-bipy ligands and water molecules to result in polyhedral blue crystals of **2**. Complex **2** was also directly synthesized by reacting $Cu(NO_3)_2 \cdot 2.5H_2O$ with 4,4′-bipy in a mole ratio of 1 : 2 under hydrothermal conditions at 120 °C for 3 days. The polyhedral blue crystals of **2** gave a yield of 67%. Anal. calcd for $C_{40}H_{62}Cu_2N_{12}O_{27}$: C, 37.83; N, 13.24; H, 4.92%; found: C, 38.69; N, 14.10; H, 4.09%.

X-Ray crystallography

All measurements were made with a Siemens SMART platform diffractometer equipped with a 1K CCD area detector, with MoKα radiation ($\lambda = 0.71073$ Å).

For complex **1**, a hemisphere of data (1271 frames at 5 cm detector distance) was collected using a narrow-frame method with scan width of 0.30% in omega and an exposure time of 30 s per frame. The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability; the maximum correction on I was $<1\%$. The data were integrated using the Siemens SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A psi scan absorption correction was applied based on the entire data set. Redundant reflections were averaged. Final cell constants were refined using 3271 reflections having $I > 10\sigma(I)$. The Laue symmetry was determined to be 4/mmm, and from the systematic absences noted the space group was shown to be either $P4(1)2(1)2$ or $P4(3)2(1)2$. The asymmetric unit consists of a one-half formula unit situated about a twofold axis.

The structure of complex **2** was solved by direct methods in SHELXTL5, and refined using full-matrix least squares on F^2. The H atoms from all water molecules could not be located from difference Fourier maps and thus were not included in the final cycle of refinement. The asymmetric unit consists of two Cu sites, four nitrates (one of which is disordered over four positions), three coordinated water molecules, seven whole water molecules and four disordered, each over four sites. The disordered nitrate was refined in four sites where each was given a site occupation factor of 0.25. The disorder in the

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Table 1 Crystal data and structure refinement for $[Cu(4,4'\text{-bipy})(NO_3)_2]$, **1**, and $[Cu(4,4'\text{bipy})_2(H_2O)_2][Cu(4,4'\text{-bipy})_2(H_2O)(NO_3)](NO_3)_3 \cdot 12H_2O$, **2**

	1	**2**
Formula	$Cu(C_{10}H_8N_2)(NO_3)_2$	$Cu_2(C_{10}H_8N_2)_4(H_2O)_{15}(NO_3)_4$
FW	343.74	1270
Temperature/K	223(2)	193(2)
Crystal system	Tetragonal	Orthorhombic
Space group	$P4_32_12$	$Fdd2$
a/Å	7.812(1)	14.3905(7)
b/Å	7.812(1)	42.019(2)
c/Å	20.232(3)	42.158(2)
U/Å^3	1234.8(3)	25 492(2)
Z	4	16
ρ_{calcd}/g cm^{-3}	1.849	1.305
μ/mm^{-1}	1.805	0.749
Reflections collected	5724	55326
Independent reflections	937	14615
R_{int}	0.0687	0.0285
Goodness-of-fit	1.035	1.097
R_1 $[I > 4\sigma(I)]$	0.0252	0.0699
wR_2 $[I > 4\sigma(I)]$	0.0654	0.2103
R_1 (all data)	0.0303	0.0797
wR_2 (all data)	0.0684	0.2233

nitrate positions is accompanied by a large disorder in four water molecules over each of four sites. Thus, there are 16 quarter water molecules in the asymmetric unit in addition to the seven whole water molecules. The geometry of all nitrate ions was constrained to be similar to each other.

Selected X-ray data for compounds **1** and **2** are given in Table 1 and selected bond lengths and angles are given in Table 2.†

Results and discussion

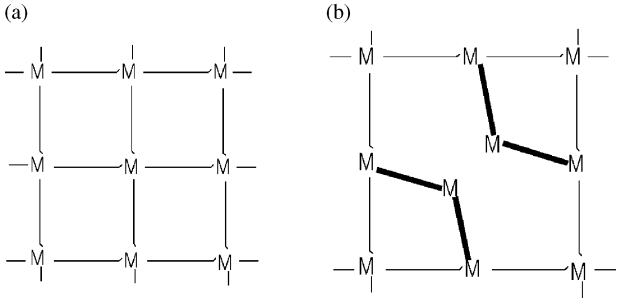
The previous report of generated OM sites from as-synthesized structures involved metal carboxylates as the secondary building unit in which the carboxylates were stronger nucleophiles than pyridyl-based functional groups.[2b] The electron-withdrawing ability of carboxylates assists the OM sites of the metal centers to be readily coordinated (including coordination from labile water molecules) so that the OM sites on the as-synthesized structures become difficult to maintain. We chose 4,4′-bipyridine as building blocks to isolate as-synthesized coordination polymers with active OM sites. 4,4′-Bipy is probably one of the most extensively studied bis-monodentate linear building units in metal-organic coordination polymers research, due to its selective functionality towards guest species and larger pore size contribution.[3] Its electronic coordination nature is relatively mild, so that the 4,4′-bipy facilitates the stabilization of OM sites in as-synthesized structures. The ideal structural model to achieve this objective implied that the metal centers adopt a square planar geometry in which they would be coordinated either by labile species, such as nitrates, and linked by 4,4′-bipy to form a 1D structure, or by 4,4′-bipy and linked perpendicularly also by 4,4′-bipy ligands to result in a 2D network with nitrates as counter anions. One of the key factors in this ideal scheme is to stop the reaction and the crystallization at the right time. The crystals after isolation should be stable enough to allow single crystal X-ray diffraction characterization.

† CCDC reference numbers 194213 (**1**) and 186585 (**2**). See http://www.rsc.org/suppdata/nj/b4/b412334d/ for crystallographic data in .cif or other electronic format.

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu(4,4'\text{-bipy})(NO_3)_2]$ and $[Cu(4,4'\text{bipy})2(H_2O)_2][Cu(4,4'\text{-bipy})_2(H_2O)(NO_3)](NO_3)_3 \cdot 12H_2O$

1			
Cu–O(1)	1.975(2)	Cu–O(1)#1	1.975(2)
Cu–N(2)#2	1.976(4)	Cu–N(1)	1.994(4)
O(1)–Cu–O(1)#1	179.55(14)	O(1)–Cu–N(2)#2	90.22(7)
O(1)#1–Cu–N(2)#2	90.22(7)	O(1)–Cu–N(1)	89.78(7)
O(1)#1–Cu–N(1)	89.77(7)	N(2)#2–Cu–N(1)	180.0
2			
Cu1–N2	2.028(4)	Cu1–N3	2.032(4)
Cu1–N4#1	2.034(4)	Cu1–N1	2.036(4)
Cu1–O1	2.367(4)	Cu1–O2	2.496(4)
Cu2–N5	2.034(5)	Cu2–N6	2.036(4)
Cu2–N8#2	2.040(4)	Cu2–N7	2.042(4)
Cu2–O3	2.350(4)	Cu2–O10	2.575(4)
N2–Cu1–N3	179.31(17)	N2–Cu1–N4#1	89.55(16)
N3–Cu1–N4#1	90.23(15)	N2–Cu1–N1	89.37(15)
N3–Cu1–N1	90.82(15)	N4#1–Cu1–N1	177.02(18)
N2–Cu1–O1	88.93(15)	N3–Cu1–O1	91.72(16)
N4#1–Cu1–O1	89.46(16)	N1–Cu1–O1	93.29(16)
N2–Cu1–O2	89.58(15)	N3–Cu1–O2	89.75(16)
N4–Cu1–O2	88.75(16)	N1–Cu1–O2	88.47(15)
O1–Cu1–O2	177.69(15)	N5–Cu2–N6	88.93(16)
N5–Cu2–N8#2	179.73(16)	N6–Cu2–N8#2	90.80(16)
N5–Cu2–N7	90.55(17)	N6–Cu2–N7	174.16(18)
N8#2–Cu2–N7	89.72(17)	N5–Cu2–O3	90.11(18)
N6–Cu2–O3	93.64(17)	N8#2–Cu2–O3	89.86(17)
N7–Cu2–O3	92.18(17)	N5–Cu2–O10	91.61(19)
N6–Cu2–O10	86.96(16)	N8–Cu2–O10	88.42(18)
N7–Cu2–O10	87.24(16)	O3–Cu2–O10	178.19(17)

Such a targeted complex was synthesized under hydrothermal conditions, from the reaction of $Cu(NO_3)_2 \cdot 2.5H_2O$ with 4,4′-bipy in the presence of iodine, resulting in complex **1**. Reactions attempted in the absence of iodine were unsuccessful under these conditions. The structure of **1** consists of one independent copper atom and a 4,4′-bipy ligand in the asymmetric unit. The copper atom has a square planar environment [with six angles of 89.77(7), 89.78(7), 90.22(7), 90.22(7), 179.6 (1) and 180.0°] and is coordinated by two trans nitrates and linked by 4,4′-bipy linear ligands, resulting in a 1D metal-organic coordination polymer (Fig. 1). Each Cu(II) metal center has two OM sites trans to the square planar motif in addition to the two replaceable labile nitrate sites. The 1D chains in crystal **1** are packed in an orientation similar to that found in BaU_2O_7, except that the chains in **1** do not share any atoms or edges with another chain.[4] In other words, the 1D chains in **1** are perpendicular to each other in the adjacent layers. This structural packing pattern in compound **1** exhibits a two-layer tetragonal cylinder packing that is not a well-documented structural pattern in coordination polymers as compared to hexagonal (honeycomb) packing of parallel cylinders and tetragonal packing of parallel cylinders.[5] The 1D chains in complex **1** are actually chiral due to the nonplanarity of 4,4′-bipy and its polar arrangement along the chains. As a



Scheme 1 Schematic of square-grid open networks.

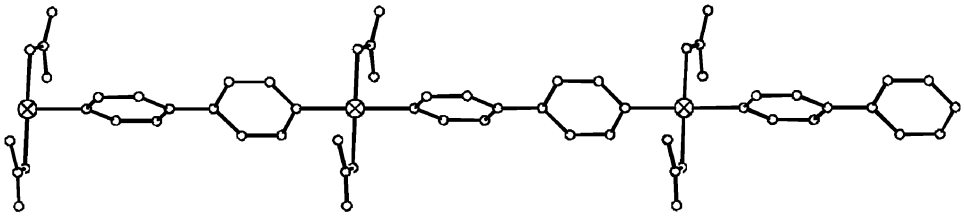


Fig. 1 Section of one linear polymeric chain in **1**.

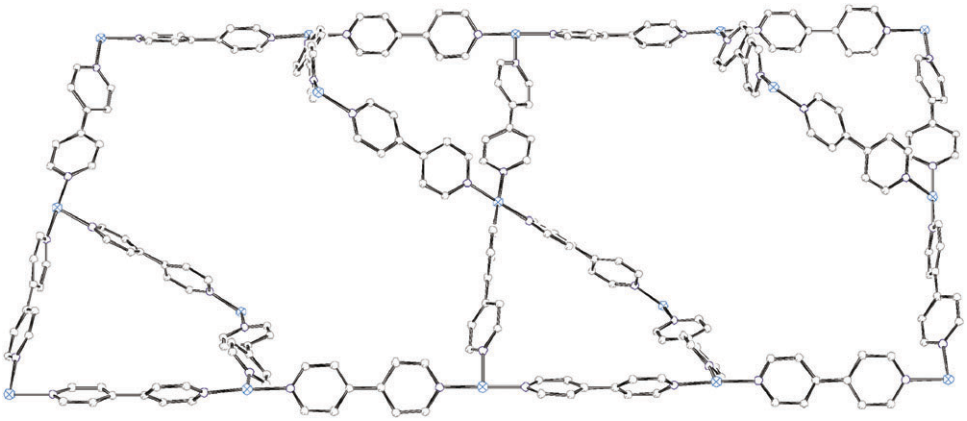


Fig. 2 View of the linkages between the two types of square grids in complex **2**.

result, the space group of compound **1** appears to be quite unusual in the context of 1D coordination polymers.

By replacing the labile nitrates with water molecules and using additional 4,4′-bipy ligands at the OM sites in complex **1**, square-grid structures [see Scheme 1(a) for a known square-grid network representation] could be built. Since the large M–4,4′-bipy–M square grid is flexible in terms of bending and twisting capabilities, the central M atom in Scheme 1(a) could be replaced by two independent M atoms, one linking the layer above and the other connecting the layer below, to form a very large square-grid network, sketched in Scheme 1(b). Hence, the square grid in Scheme 1(a) could "break" in Scheme 1(b), to become a complementary square-grid building unit for larger grid dimensions. The 2D network is transformed into a 3D open-framework structure. Although this scheme is only one of the possible structural changes, the self-assembly process produced the corresponding new guest-inclusion metal-organic polymer: $\{[Cu(4,4'\text{-bipy})_2(H_2O)_2][Cu(4,4'\text{-bipy})_2(H_2O)(NO_3)]\}(NO_3)_3 \cdot 12H_2O$, **2**.

Complex **2** was obtained by allowing purple crystals of complex **1** to stand in solution in the presence of 4,4′-bipy molecules overnight. The labile nitrates and the active OM sites in **1** were replaced by additional 4,4′-bipy ligands and water molecules to result in polyhedral blue crystals of **2**. Complex **2** was also directly synthesized by reacting $Cu(NO_3)_2 \cdot 2.5H_2O$ with 4,4′-bipy under hydrothermal conditions.

The structure of complex **2** consists of two independent Cu-centered structural units. Cu1 has an octahedral environment

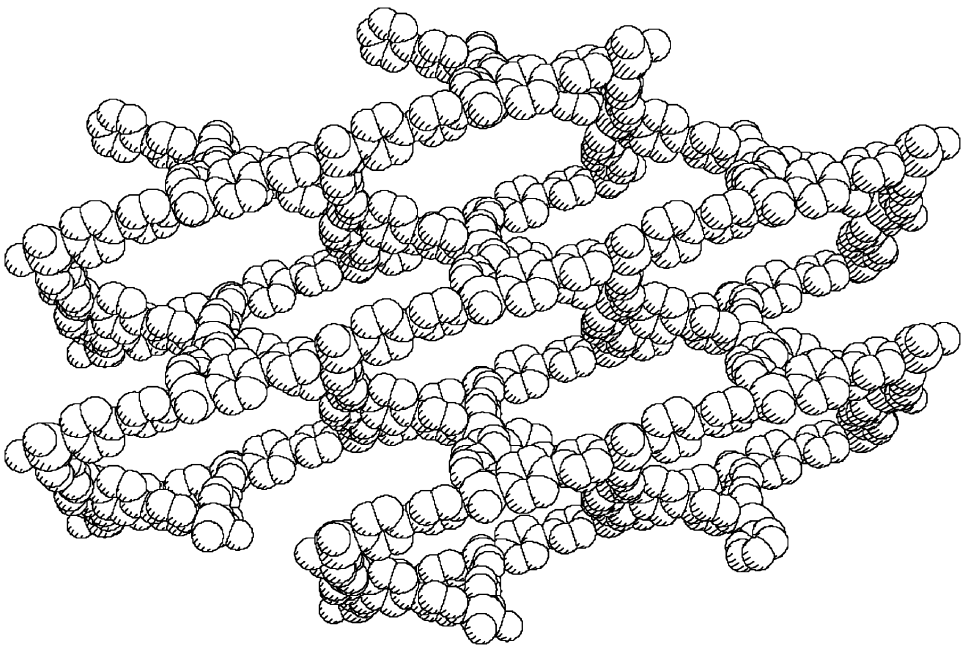


Fig. 3 A space-filling view of the 3D open-framework in complex **2** along the [010] direction.

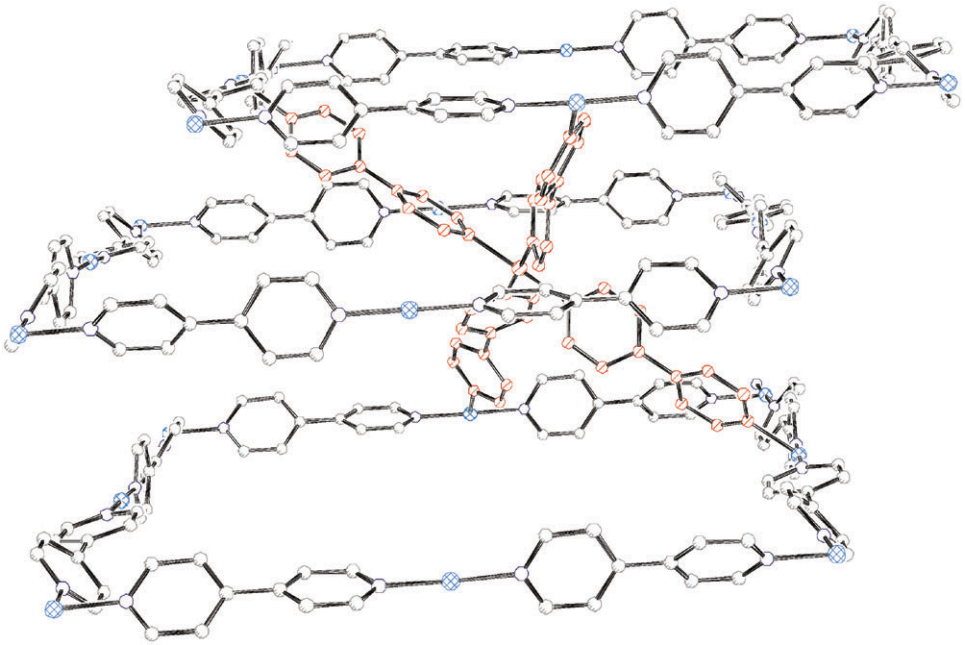


Fig. 4 View of the 3D open-framework linkages in complex **2**. The "bending" part of the square grid is in red. Copper atoms are in blue.

surrounded by four 4,4′-bipy at the equatorial positions and two water molecules at the axial positions. It has a weak interaction to oxygen atom 2 [2.496(4) Å]. Cu2 is also in an octahedral environment and is coordinated by four 4,4′-bipy and a water molecule. It has a very long coordination with a nitrate oxygen atom [2.575(4) Å], which distinguishes it from Cu1. Both Cu1 and Cu2 are clearly showing Jahn–Teller distortions. Each independent network has two types of square grids with copper atom separations of 11.105 × 11.137 $Å^2$, and 22.208 × 22.273 $Å^2$. As shown in Fig. 2, the two types of square-grid linkages are the same as those described in Scheme 1(b).

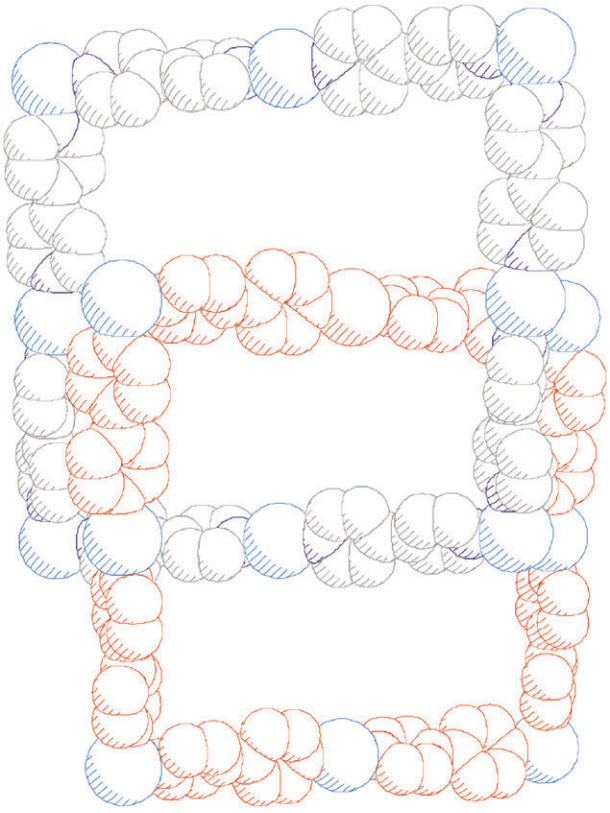


Fig. 5 View of the onefold interpenetrating network in **2**. Copper atoms are in blue.

The square grid in each independent network extends into a 3D open-framework with channels in the three directions (Fig. 3). The larger square-grid networks in the two independent networks are parallel to each other and each 3D network is linked *via* the complementary square grid (Fig. 4), leading to a twofold mutual interpenetration between the large square-grid networks (Fig. 5). The two 3D networks with minimum interpenetration enable this 3D open-channel structure to accommodate a large number of water molecules and nitrate anions. There are 64 nitrates and 192 water molecules included in a unit cell volume of the structure.

Alternatively, the structure of complex **2** may be described as a 3D $4^2.8^4$ topology net from covalently bonded square nodes. Although the 3D $4^2..8^4$ topology net has been reported for coordination polymers recently,[6] and a $4^2.8^4$ network was observed in hydrogen-bonded networks,[7] complex **2** is, to the best of our knowledge, the first synthesized 3D interpenetrating $4^2.8^4$ network coordination polymer. In comparison with known Cu^{2+}–4,4′-bipy coordination polymers listed in Table 3, the single 4,4′-bipy ligand-coordinated copper(II) complexes reported here are noteworthy and unique.

It is important to note that the noncentrosymmetric feature in coordination polymer **1** is maintained in the 3D coordination polymer **2**, implying that the self-assembly process from complex **1** to complex **2** favors the reactivity of the unsaturated active metal sites rather than reorganization.

Table 3 Known Cu(II)-4,4′-bipy coordination polymers[a] characterized by single crystal structure data collected from the CCDC[b]

Compound	Structure type	Ref.
$[Cu(4,4'\text{-bipy})_2(H_2O)_2](ClO_4)_4(4,4'\text{-}H_2bipy)$	2D	8
$[Cu(4,4'\text{-bipy})(H_2O)_3(SO_4)]\cdot 2H_2O$	1D	9
$[Cu(4,4'\text{-bipy})_2(NO_3)_2](paba)_3$	2D	10
$[Cu(4,4'\text{-bipy})_2(H_2O)_2(FBF_3)_2](4,4'\text{-bipy})$	2D	11
$[Cu(4,4'\text{-bipy})_2(AF_6)]\cdot 8H_2O$ (A = Si, Ge)	3D	12
$[Cu(4,4'\text{-bipy})_2(H_2O)_2](AF_6)$ (A = Si, Ge)	2D	12

[a] Mixed-ligand, mixed-solvent, and mixed-anions are excluded. [b] Cambridge Crystallographic Data Centre.

Thermal analysis revealed that complex **2** lost water molecules, including structural water molecules, between 55 and 110 °C (~22%), and two 4,4′-bipy molecules at 235 °C (~25%). The framework of complex **2** was completely decomposed at 335 °C. The loss of structural water molecules at lower temperature indicates that the framework structure of complex **2** is not very stable, which is consistent with the X-ray diffraction results. In order to improve the structural stability of complex **2**, the replacement of coordinating water molecules would be a logical approach, which would result in a new compound with a 3D structure. Several synthetic attempts have been made in our laboratory but they were not successful yet.

In summary, this work demonstrated the synthesis of a new metastable OM -site-containing 1D coordination polymer and a novel 3D interpenetrating $4^2.8^4$ network constructed through the utilization of 4,4′-bipy ligands. Although many Cu^{2+}–4,4′-bipy coordination polymers are known (see Table 3),[8–12] the complementary interpenetrating 3D network in complex **2** is unprecedented.

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