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Article

Three New Heterothiometallic Cluster Polymers with Fascinating Topologies

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Three new heterothiometallic cluster polymers with fascinating topologies have been synthesized by the self-assembly of preformed heterothiometallic cluster monomers and appropriate ligands. Reaction of the monomeric cubic-shaped cluster $[Et_4N]_3[MoOS_3Cu_3I_4]$ with the D_{2h} symmetry rigid bidentate 4,4′-bipy (4,4′-bipyridine) gave a two-dimensional (2D) layer compound $[Mo_2O_2S_6Cu_6I_2(4,4'\text{-bipy})_3(H_2O)]_n$ (**1**); the assembly of pentanuclear cluster monomer $[Et_4N]_4[WS_4Cu_4I_6]$ with C_s-symmetrical bpe (1,2-bis(4-pyridyl)ethane) afforded a 2D layer compound $[WS_4Cu_4I_2(bpe)_3(H_2O)]_n$ (**2**), and the assembly of heptanuclear cluster monomer $[Et_4N]_4[WS_4Cu_6I_8]$ with D_{3h} symmetry trigonal planar ligand timtz (2, 4, 6-tri(1*H*-imidazol-1-yl)-1, 3, 5-triazine) afforded a three-dimensional (3D) compound $[WS_4Cu_6I_4(timtz)_{8/3}(H_2O)_{12}]_n$ (**3**). X-ray crystallographic analysis reveals that **1** crystallizes in trigonal space group $R\bar{3}c$ with 2D 3^6-**hxl** net which is the first heterothiometallic superamolecular structure based on a twin cubic-shaped cluster monomer and also the first example of 4,4′-bipy-connected compound of this net. **2** crystallizes in tetragonal space group $P4_2$ with distorted 2D 3^6-**hxl** net which is the first flexible-ligand-based compound of this topology; while **3** has a 3D net with the high symmetry of cubic space group $I\bar{4}3d$, and has a novel α-C_3N_4 topology, which is the maximum symmetry for this net topology. The gas sorption isotherm was measured for **3** to exhibit type-III sorption behavior.

Introduction

The designed syntheses of metal organic frameworks (MOFs) have attracted great attention in recent years because of not only their intriguing variety of architectures and topologies[1] but also their potential applications in catalysis,[2] magnetism,[3] nonlinear optics,[4] and chemical absorption.[5] SBUs (Secondary Building Units), possessing necessary shape and geometry, polycoordinating sites, and desired directionality, are widely used to design and construct the predefined building units into network structures with expected topologies.[6] Many topologically interesting

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structures have been discussed in comprehensive reviews by Yaghi,[7] Ciani, and co-workers.[8]

So far, the construction of cluster-containing supramolecular compounds has mostly focused on using metal−oxygen clusters as buliding blocks. There have only been a few reports on the supramolecular compounds with metal−sulfur clusters as SBUs. Meanwhile, the chemistry of Mo(W)/Cu/S heterothiometallic clusters have remained an active research area because of their importance in advanced materials, biological processes, and catalytic reactions.[9] On the basis of these two facts, our group has been interested in the assembly of cluster-based supramolecular compounds using preformed Mo(W)/Cu/S clusters as SBUs in search of new cluster compounds with fascinating aesthetic architectures and/or useful physical properties.[10] In these compounds, the Mo(W)/Cu/S cluster SBUs are normally connected by linear bridging ligands such as 4,4′-bipy(4,4′-bipyridine), bpe (1,2-bis(4-pyridyl)ethane), and bppe (1,3-bis(4-pyridyl)propane). Until recently, few trigonal planar ligands were chosen to construct Mo(W)/Cu/S cluster-based compounds, and only one two-dimensional (2D) polymer with [MoS_3Cu_3] as SBUs and tpt (tpt = 2,4,6-tri(4-pyridyl)-1,3,5-triazine) as linkers was synthesized.[11]

Both the fixed geometry of the preformed clusters SBUs and the ligand symmetry can affect the formation of cluster-based structures.[7,8,12] So various architectures with intriguing topologies can be constructed by rational design of preformed clusters and appropriate ligands. To explore this field, we selected three kinds of different organic ligands with different symmetries: 4,4′-bipy (D_{2h} symmetry), bpe (C_s symmetry), and rigid timtz (D_{3h} symmetry), as linkers to assemble Mo(W)/Cu/S heterothiometallic cluster polymers. The self-assembly reaction of the monomeric cubic-shaped cluster $[Et_4N]_3[MoOS_3Cu_3I_4]$[13] with the D_{2h} symmetry rigid bisdentate 4,4′-bipy gave a 2D $[Mo_2O_2S_6Cu_6I_2(4,4'\text{-bipy})_3(H_2O)]_n$ (**1**) with an octanuclear twin cubic-shaped cluster as SBUs; the assembly of the pentanuclear cluster $[Et_4N]_4[WS_4Cu_4I_6]$[14] with C_s-symmetry bpe afforded a saddle-shaped 2D layer compound $[WS_4Cu_4I_2(bpe)_3(H_2O)]_n$ (**2**), and the assembly of the heptanuclear cluster monomer $[Et_4N]_4[WS_4Cu_6I_8]$[15] with D_{3h} symmetry trigonal planar ligand timtz afforded a three-dimensional (3D) compound $[WS_4Cu_6I_4(timtz)_{8/3}(H_2O)_{12}]_n$ (**3**).

Experimental Section

Materials and Methods. The starting materials $(NH_4)_2WS_4$ and $(NH_4)_2MoO_2S_2$ were prepared according to the literature.[16] Ligand timtz was prepared according to literature method,[17] and other chemicals were used as commercially available. The IR absorption spectra of the complexes were recorded in the range of 400−4000 cm^{-1} by means of a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). C and H analyses were carried out with a Perkin-Elmer 240C elemental analyzer. X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (0.15418 nm), in which the X-ray tube was operated at 40 kV and 40 mA. The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin-Elmer thermogravimetric analyzer Pyris 1 TGA using a heating rate of 20 K min^{-1} under a N_2 atmosphere. Brunauer−Emmett−Teller (BET) surface areas and pore-size distributions were measured using a Micromeritics ASAP2000 adsorption analyzer.

Synthesis of $[Mo_2O_2S_6Cu_6I_2(4,4'\text{-bipy})_3(H_2O)]_n$ (1). To a red solution of $[Et_4N]_3[MoOS_3Cu_3I_4]$ (648 mg, 0.5 mmol) in MeCN (4 mL) was added a *N*,*N*-dimethylformamide (DMF, 2 mL) solution containing 4,4′-bipy (156 mg, 1 mmol), and the final mixture was sealed in a 15 mL PTFE-lined stainless-steel acid digestion bomb and heated at 100 °C for 2 days. Red prism-shaped single crystals suitable for X-ray diffraction were obtained several days later in 46% yield. Elemental analysis calcd (%) for $C_{30}H_{26}Cu_6I_2N_6Mo_2O_3S_6$: C 23.43, H 1.70, N 5.46; found: C 23.49, H 1.78, N 5.52. IR (KBr, cm^{-1}): 3439 (s), 3040 (w), 1599 (s), 1527 (m), 1482 (s), 1406 (s), 1214 (m), 1060 (m), 854 (w), 815 (s), 630 (m), 432 (w).

Synthesis of $[WS_4Cu_4I_2(bpe)_3(H_2O)]_n$ (2). To a red solution of $[Et_4N]_4[WS_4Cu_4I_6]$ (924 mg, 0.5 mmol) in MeCN (4 mL) was added a DMF (2 mL) solution containing bpe (276 mg, 1.5 mmol), and the final mixture was sealed in a 15 mL PTFE-lined stainless-steel acid digestion bomb and heated at 100 °C for 2 days. Red prism-shaped single crystals suitable for X-ray diffraction were obtained several days later in 72% yield. Elemental analysis calcd (%) for $C_{36}H_{38}Cu_4I_2N_6WOS_4$: C 31.09, H 2.75, N 6.04; found: C 31.15, H 2.82, N 6.12. IR (KBr, cm^{-1}): 3441 (m), 3027 (w), 1608 (s), 1556 (w), 1423 (s), 1223 (m), 1067 (m), 1018 (m), 819 (s), 523 (w), 431 (m).

Synthesis of $[WS_4Cu_6I_4(timtz)_{8/3}(H_2O)_{12}]_n$ (3). To a red solution of $[Et_4N]_4[WS_4Cu_4I_8]$ (1051 mg, 0.5 mmol) in MeCN (4 mL) was added a DMF (2 mL) solution containing timtz (558 mg, 2.0 mmol) ligand, and the final mixture was sealed in a 15 mL PTFE-lined stainless-steel acid digestion bomb and heated at 75 °C for 2 days. Red prism-shaped single crystals suitable for X-ray diffraction were obtained several days later in 32% yield. Elemental analysis calcd (%) for $C_{32}H_{48}Cu_6I_4N_{24}O_{12}S_4W$: C 17.78, H 2.24, N 15.55; found: C 17.89, H 2.31, N 15.62. IR (KBr, cm^{-1}): 3421(w), 3126(w), 1652(s), 1595(s), 1542(m),

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Table 1. Crystallographic Data and Structure Refinement Details for Complexes **1**−**3**

compound	1	2	3
formula	$C_{30}H_{26}Cu_6I_2Mo_2N_6O_3S_6$	$C_{36}H_{38}Cu_4I_2N_6OS_4W$	$C_{32}H_{48}Cu_6I_4N_{24}O_{12}S_4W$
formula weight	1537.85	1390.77	2161.87
crystal system	trigonal	tetragonal	cubic
space group	$R\bar{3}c$	$P4_2$	$I\bar{4}3d$
a (Å)	13.4384(14)	12.6773(7)	30.361(3)
b (Å)	13.4384(14)	12.6773(6)	30.361(3)
c (Å)	40.600(7)	13.2398(14)	30.361(3)
α (deg)	90.00	90.00	90.00
β (deg)	90.00	90.00	90.00
γ (deg)	120.00	90.00	90.00
V (Å^3)	6349.7(14)	2127.8(3)	27986(5)
cryst size (mm)	0.28 × 0.22 × 0.20	0.30 × 0.26 × 0.24	0.26 × 0.24 × 0.22
Z	6	2	12
D_c (g cm^{-3})	2.413	2.171	1.539
μ(Mo Ka)(mm^{-1})	5.321	6.344	4.030
F(000)	4392	1328	12336
theta min-max (deg)	2.02, 25.99	1.61, 25.98	1.90, 25.99
tot., uniq. data,	10744, 1394	11810, 4163	72278, 4597
$R_{(\mathrm{int})}$	0.0625	0.0495	0.0819
observed data [I > 2sigma(I)]	1011	3657	4270
Nref, Npar	1394, 84	4163, 245	4597, 233
R, wR2 (all data)	0.1007, 0.2717	0.0621, 0.1223	0.0523, 0.1067
S	1.073	1.148	1.059
min and max resd dens (e·Å^{-3})	−2.343, 1.813	−1.710, 1.335	−0.862, 0.698

1471(vs), 1434(vs), 1319(m), 1221(m), 1097(m), 1069(s), 1014(s), 976(w), 948(w), 802(s), 753(m), 644(m), 609(m), 446(w).

X-ray Crystallography. X-ray crystallographic data of **1**−**3** were collected on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values using the SHELXTL (version 6.10) package of crystallographic software. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The relevant crystallographic data are presented in Table 1, while the selected bond lengths and angles are given in Supporting Information, Table S1.

Results and Discussion

Structure of Compound 1. The fundamental building block of **1** is a cubic-shaped cluster monomer [$MoOS_3Cu_3I$]. The [$MoOS_3Cu_3I$] cluster unit lies across a 3-fold axis that runs through Mo1, O1, and Cu1 atoms; all other atoms lie on general positions (except the intercalated water molecule, which lies on a site of 32 symmetry). The Mo−O bond length is 1.68(2) Å, while the three Mo−S bond lengths are the same [2.301(3) Å], consistent with the expected arrangement of one Mo═O double bond and three Mo−S single bonds. Both Mo and Cu atoms are tetrahedrally coordinated. Every Cu atom is coordinated to two S atoms, one N atom, and one I atom. One Mo atom, three S atoms, three Cu atoms, and one I atom locate in cube vertices (Supporting Information, Figure S1). Two cubic-shaped [$MoOS_3Cu_3I$] cluster monomers dimerized into a twin cubic-like unit [$Mo_2O_2S_6Cu_6I_2$] by sharing one I−I bridge, which acts as SBU. Each SBU is linked to six others by six bidentate 4,4′-bipy ligands to form a snowflake-liked shape (Figure 1). In turn, each SBU is linked to another one, by a 4,4′-bipy, thus yielding a 2D layer structure (Figure 2). Figure 3 shows the view of compound **1** along b axis. Topologically, the SBUs can be regarded as 6-connected nodes, and the whole structure may be described as a 2D grid of 3^6-**hxl** net (Supporting Information, Figure S2). Though examples of such a grid have been previously described,[18] none were formed with 4,4′-bipy-connected compounds. **1** is also the first compound that holds a twin cubic-shaped heterothiometallic cluster monomers as SBUs.

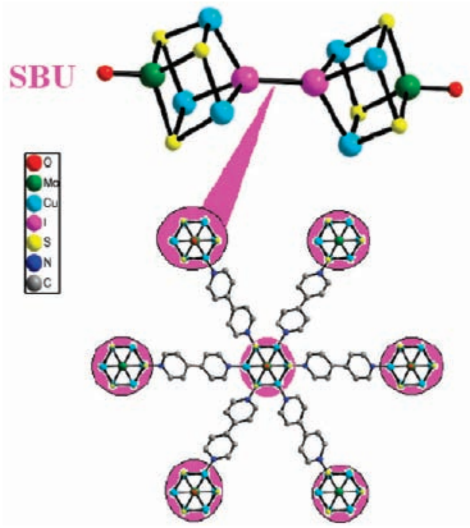

Figure 1. View of a snowflake-like compound **1** where each [$Mo_2O_2S_6Cu_6I_2$] unit is surrounded by six 4,4′-bipy ligands.

Structure of Compound 2. Compound **2** consists of the saddle-shaped [$WS_4Cu_4I_2$] SBUs. The central W1 atom of the SBU lies on a 2-fold axis; all other framework atoms

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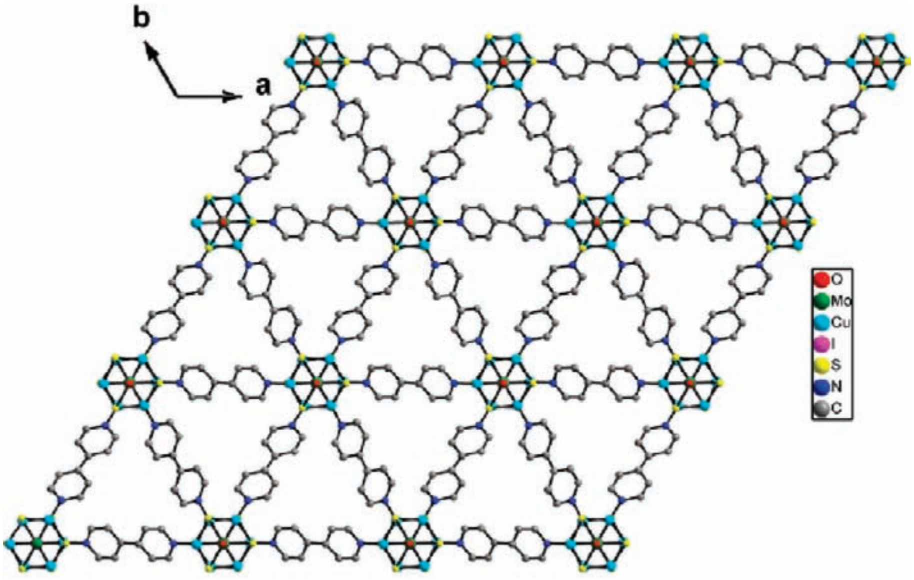

Figure 2. Schematic representation of the 2D 3^6-**hxl** net of compound **1**.

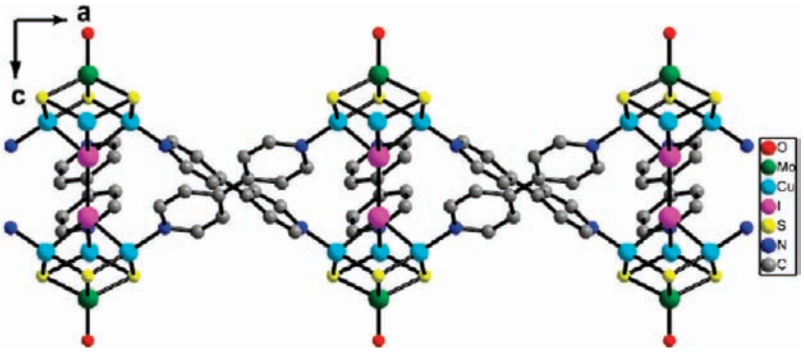

Figure 3. Side view of a layer of **1**, as seen perpendicular to the *ac*-plane.

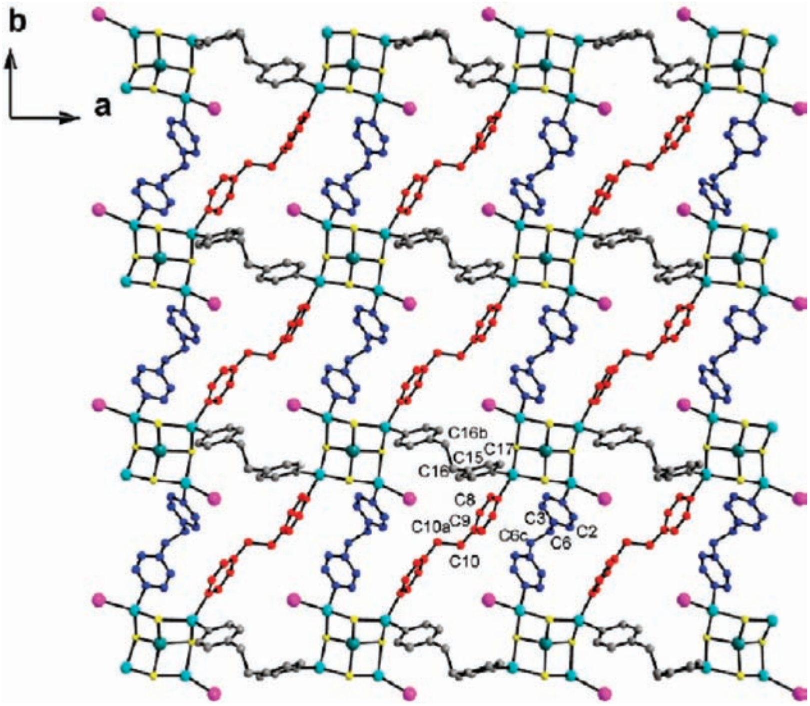

Figure 4. View, down the *c*-axis, of a layer of compound **2** (symmetry code: $a = 1 - x, -y, z$; $b = 1 - x, 1 - y, z$; $c = 2 - x, -y, z$).

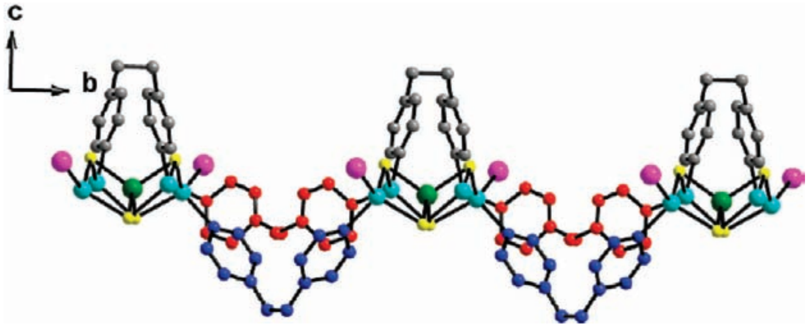

Figure 5. View of compound **2** along *a* axis.

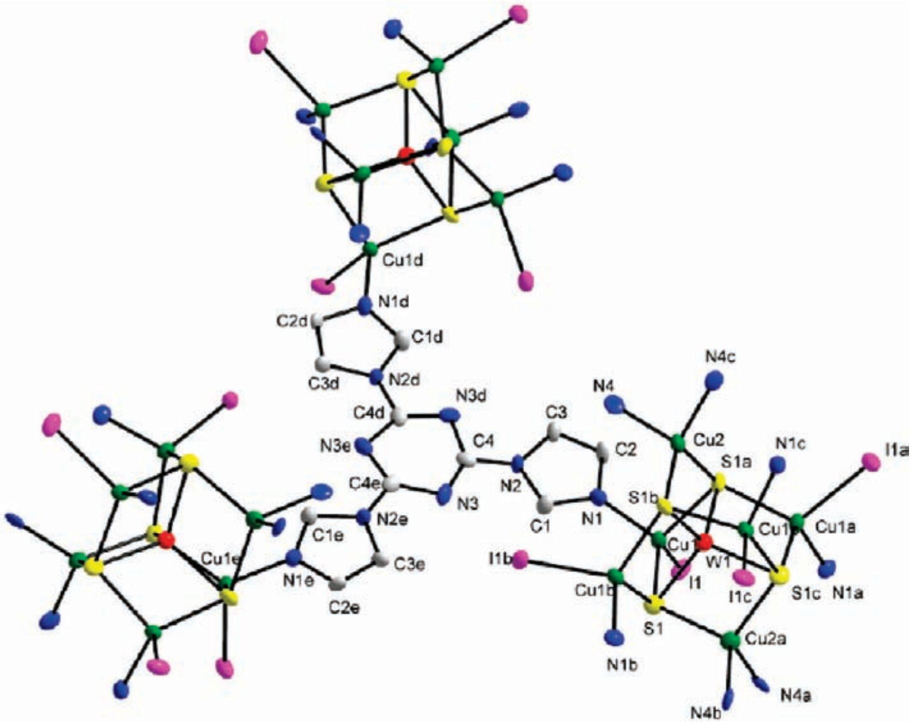

Figure 6. Coordination environment of **3** with 30% ellipsoid probability (hydrogen atoms and water molecules are omitted for clarity). symmetry code: $a = 0\ 0.25 - x, 0.25 + z, 1.75 - y$; $b = 0\ 0.25 - x, 1.75 - z, -0.25 + y$; $c = x, 2 - y, 1.5 - z$; $d = -0.5 + y, 1.5 - z, 1 - x$; $e = 1 - z, 0.5 + x, 1.5 - y$.

lie on general positions. The structure contains two kinds of copper atoms: Cu(1) and Cu(2). Cu(1) atoms are tetrahedrally coordinated by two μ_3-S atoms, one terminal I atom, and one N atom from one bridging bpe ligand, while Cu(2) atoms are tetrahedrally coordinated by two μ_3-S atoms and two N atoms from two bridging bpe ligands (Supporting Information, Figure S3). The lattice also contains intercalated water molecules, each of which lie above one face of a SBU, on the same 2-fold axis as the W1 atom, and hydrogen bonds to the two S2 atoms of the cluster (Supporting Information, Table S2).

The four Cu(I) centers in the SBU are linked by six bpe ligands and form a 2D layer network (Figure 4). The six bpe ligands can be sorted into three types according to the torsion angles and dihedral angles between the two phenyl rings of the bpe ligands, which are labeled by red, gray, and blue. The torsion angles of C8—C9—C10—C10a, C17—C15—C16—C16b, and C2—C3—C6—C6c are 94.4(12)°, 79.3(12)°, and 116.1(12)°, respectively, and the angles between the two phenyl rings of the bpe ligands are 27.84(36), 32.56(33), and 63.10(27)°, respectively. A view of compound **2** along the *a* axis is shown in Figure 5. From a topological perspective, the SBU also acts as a 6-connected node. The different bend tendency of the two phenyl rings of the bpe ligands results in a distorted 3^6-**hxl** net with an angle of 45° (Supporting Information, Figure S4). As far as we known, linkers used in the compounds with 2D 3^6-**hxl** net are all rigid or semirigid ligands, and the triangles are all equilateral.[18] No flexible ligand has been reported to construct such a topological structure. **2** represents the first distorted 3^6-**hxl** net by using flexible ligand bpe as linkers.

Structure of Compound 3. Octahedral $[WS_4Cu_6]$ clusters, in which a WS_4 group is surrounded by six copper atoms (Figure 7a), may be regarded as the SBUs in polymer **3**. The central W atom of this cluster lies on a 4-fold rotary inversion axis, while there are two different copper atoms: Cu(1) lies on a general position while Cu(2) lies on a 2-fold axis. All other atoms lie on general

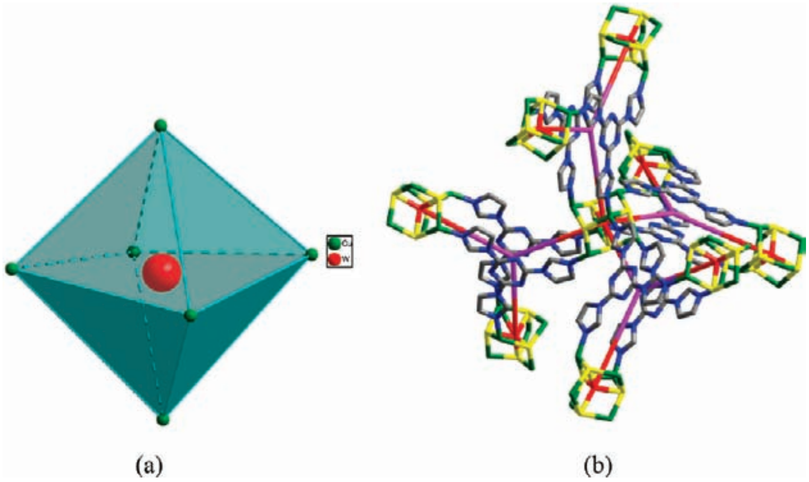

Figure 7. (a) Representation of the $[WCu_6]$ octahedron, (b) the local connectivity in **3**, highlighting the 3-connecting pairs of ligands, and the 4-connecting clusters (I and H atoms were omitted for clarity).

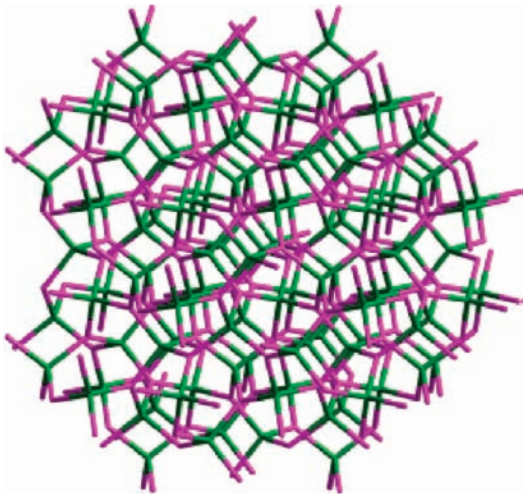

Figure 8. Overall α-C_3N_4 (**ctn**) topology of compound **3**. Green and purple nodes represent cluster fragment $[WS_4Cu_6I_4]$ units and the tridentate timtz ligands, respectively.

positions, although the timtz ligand lies on a 3-fold axis, which passes through the central triazine ring. Each S atom in the cluster acts as a tetradentate ligand binding with three Cu atoms and one W atom. Two axial Cu(2) atoms and four equatorial Cu(1) atoms form an octahedron with the distance of Cu(2)−W and Cu(1)−W being 2.6950(14) Å and 2.7327(9) Å, respectively, and the Cu(2)−W−Cu(1), Cu(1)−W−Cu(1), and Cu(2)−W−Cu(2) bond angles being 85.755(19), 90.314(3), 180.0°, respectively. Cu(1) and Cu(2) atoms adopt distorted tetrahedral coordinations. Cu(1) atoms bind with two S atoms, one terminal I atom, and one N atom from the timtz ligand, while Cu(2) atoms each coordinate with two S atoms and two N atoms from the two timtz ligands (Figure 6). The two timtz ligands lie face-to-face connecting with three SBUs, and each SBU links to four of these timtz ligand pairs. The overall topology is therefore a 3,4-connected net, with each ligand pair acting as the 3-connecting node, and each SBU acting as a 4-connecting node. The overall topology is the same as the α-C_3N_4 (or **ctn**) network (Figure 7b, 8).[19] The Schläfli symbol is $(8^3)_4(8^6)_3$. Free water molecules filled in the channels. There are abundant hydrogen bonds between these water molecules (Supporting Information, Table S2 and Figure S5). Notably, the structure of **3** has the high symmetry of $I\bar{4}3d$, which is the maximum symmetry for this net topology. There are very few examples of this net, with one being the structure of a Cu^I coordination polymer of the trigonal 2,4,6-tri-(4-pyridyl)-1,3,5-triazine ligand.[20]

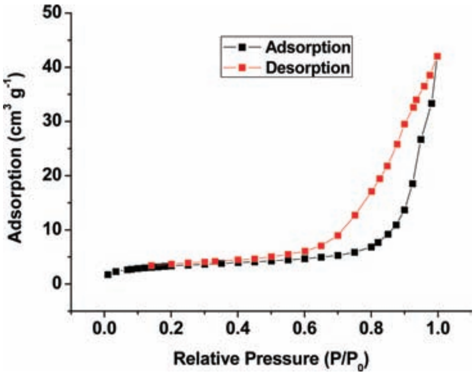

Figure 9. N_2 absorption isotherms of compound **3** at 77 K.

N_2 Sorption Properties of Compound 3. The total void value of the channels without water guests is estimated (by Platon[21]) to be 14921.3 $Å^3$, approximately 53.3% of the total crystal volume of 27987.0 $Å^3$. To evaluate the permanent porosity of the framework of compound **3**, nitrogen sorption isotherm measurements (Figure 9) were performed on a desolvated crystalline sample at 77 K. It shows a typical type-III gas sorption behavior[22] and an N_2 uptake of approximately 42.02 cm^3 (STP)/g, with a Langmuir surface area of 16.74 m^2/g and BET surface area of 12.02 m^2/g.

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Thermal Analysis and XRD Results. To characterize the compounds more fully in terms of thermal stability, their thermal behaviors were studied by TGA (Supporting Information, Figure S6). TGA reveals a weight loss of 1.13% and 1.25% for compounds **1** and **2** in the region of 20−80 °C, respectively, consistent with the loss of lattice water molecules from the channels of compounds **1** and **2**. A plateau region in the temperature range of 80−220 °C indicates that the molecular architecture of the compounds **1** and **2** can be stable up to 220 °C in the absence of guests. Compound **3** loses 9.33% in the region of 20−360 °C, consistent with the loss of lattice water molecules from the channels of compound **3**. The purity of compounds **1**−**3** is confirmed by powder XRD analyses, in which the main peaks of experimental spectra of **1**−**3** are almost consistent with its simulated spectrum (Supporting Information, Figures S7−S9).

Conclusions

In summary, we synthesized three unprecedented 2D or 3D supramolecular arrays **1**−**3** from reactions of the preformed clusters with different ligands respectively: rigid 4,4′-bipy (D_{2h}), flexible bpe (C_s), and rigid trigonal planar ligand timtz (D_{3h}). The [$Mo_2O_2S_6Cu_6$] core in **1**, [WS_4Cu_4] core in **2**, and [WS_4Cu_6] core in **3** were retained and served as 6, 6, and 4-connecting node respectively. To the best of our knowledge, **1** represents the first heterothiometallic supramolecular polymer which holds twin cubic-shaped cluster monomers as SBUs and also the first example of 4,4′-bipy-connected 2D 3^6-**hxl** net. **2** is the first distorted 3^6-**hxl** net connected by flexible ligand, and **3** has a novel α-C_3N_4 (or **ctn**) topology. These interesting structures of **1**−**3** proved that many fascinating topologies can be constructed by rational combination of SBUs with suitable organic ligands. This work is continuing.

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Supporting Information Available: TGA, XRD patterns, additional figures and X-ray crystallographic files in CIF format for the structure determination of compounds **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.