Inorg. Chem. **2008**, *47*, 8197−8203

Inorganic Chemistry

Article

Cu_6S_4 Cluster Based Twelve-Connected Face-Centered Cubic and $Cu_{19}I_4S_{12}$ Cluster Based Fourteen-Connected Body-Centered Cubic Topological Coordination Polymers

Zheng-Ming Hao, Rui-Qin Fang, Hai-Shun Wu, and Xian-Ming Zhang*

School of Chemistry & Material Science, Shanxi Normal University, Linfen, Shanxi 041004, China

Received April 20, 2008

Hydrothermal reaction of $Cu(MeCO_2)_2$, (4-pyridylthio)acetic acid and NH_4SCN resulted in a twelve-connected face-centered cubic topological metal-organic framework $[Cu_3(pdt)_2(CN)]$ (pdt = pyridinethiolate) in which Cu_6S_4 clusters act as twelve-connected nodes and pyridine rings and cyanides act as connectors. As an extension, an unprecedented fourteen-connected body-centered cubic coordination polymer $[Cu_{19}I_4(pdt)_{12}(SH)_3]$ has been synthesized by three methods, in which nanosized chiral $Cu_{19}I_4S_{12}$ clusters act as fourteen-connected nodes and triple pyridine rings and hydrosulfides act as connectors. The in situ S−C(sp^3), S−C(sp^2), and S−C(sp) cleavage reactions have been observed in the work.

Introduction

Metal-organic frameworks are of great current interest because of intriguing topologies and possible applications in gas storage, catalysis, luminescence, and Nonlinear Optical materials.[1] The classification of structures by Wells lays the foundation of the general understanding of inorganic solids, as well as coordination polymers.[2] It appears that for the majority of the coordination polymers, there are well-known structural prototypes in elemental or binary inorganic solids, such as diamond, α-Po, boracite, CaB_6, feldspar, NbO, perovskite, Pt_3O_4, PtS, pyrite, quartz, rutile, sodalite, $SrSi_2$, tungsten bronze, CsCl, and fluorite, which have further stimulated the interest in mimicking topological types of inorganic solids by coordination polymers.[3,4] It should be noted that, of the structural types commonly found in coordination polymers, the majority are based on three-, four- and six-connected topologies with single *d*-and *f*-block metal centers as nodes. Examples of seven-connected, eight-connected, nine-connected, and twelve-connected coordination frameworks are extremely rare.[5−12] Recently, metal clusters and supramolecular building blocks (SBBs) in place

---

* To whom correspondence should be addressed. E-mail: zhangxm@dns.sxnu.edu.cn. Fax: +86 357 2051402. Phone: +86 357 2051402.

(1) For recent reviews, see:(a) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474–484. (b) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117–138. (c) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460–1494. (d) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew Chem., Int. Ed.* **1999**, *38*, 2638–2684. (e) Fujita, M. *Acc. Chem. Res.* **1998**, *32*, 53–61. (f) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629–1658. (g) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Coord. Chem. Rev.* **2003**, *246*, 247–289. (h) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375. (i) Ferey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217–225.

(2) Wells, A. F. *Three-Dimensional Nets and Polyhedra*; Wiley: New York, 1977.

(3) (a) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705–714. (b) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176–182.

(4) *RCSR and EPINET*, two sources of crystalline networks; the associated website are as follows: http://okeeffe-ws1.la.asu.edu/RCSR/home.htm and http://epinet.anu.edu.au.

(5) Hill, R. J.; Long, D.-L.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Acc. Chem. Res.* **2005**, *38*, 337–350.

(6) For eight-connected **bcu** networks, see:(a) Lu, J.; Harrison, W. T. A.; Jacobson, A. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2557–2559. (b) Long, D.-L.; Blake, A. J.; Champness, N. R.; Wilson, C.; Schröder, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2443–2447. (c) Long, D.-L.; Hill, R. J.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Proserpio, D. M.; Wilson, C.; Schröder, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1851–1854. (d) Luo, T. T.; Tsai, H. L.; Yang, S. L.; Liu, Y. H.; Yadav, R. D.; Su, C. C.; Ueng, C. H.; Lin, L. G.; Lu, K. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 6063–6067. (e) Fang, Q.-R.; Zhu, G.-S.; Jin, Z.; Xue, M.; Wei, X.; Wang, D.-J.; Qiu, S.-L. *Angew. Chem., Int. Ed.* **2006**, *45*, 6126–6130.

(7) (a) Lan, Y.-Q.; Wang, X.-L.; Li, S.-L.; Su, Z.-M.; Shao, K.-Z.; Wang, E.-B. 4863−4865. (b) Morris, J.-J.; Noll, B.-C. *Chem. Commun.* **2007**, 5191–5193. (c) Zou, W.-Q.; Wang, M.-S.; Li, Y.; Wu, A.-Q.; Zheng, F.-K.; Chen, Q.-Y.; Guo, G.-C.; Huang, J.-S. *Inorg. Chem.* **2007**, *46*, 6852–6854. (d) Liu, C.-M.; Gao, S.; Zhang, D.-Q.; Zhu, D.-B. *Cryst. Growth Des.* **2007**, *7*, 1312–1317. (e) Qu, X.-S.; Xu, L.; Gao, G.-G.; Li, F.-Y.; Yang, Y.-Y. *Inorg. Chem.* **2007**, *46*, 4775–4777. (f) Zou, R.-Q.; Zhong, R.-Q.; Du, M.; Kiyobayashi, T.; Xu, Q. *Chem. Commun.* **2007**, 2467–2469. (g) Chun, H.; Kim, D.; Dybtsev, D. N.; Kim, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 971–974. (h) Zhang, J.; Kang, Y.; Zhang, J.; Li, Z.-J.; Qin, Y.-Y.; Yao, Y.-G. *Eur. J. Inorg. Chem.* **2006**, *11*, 2253–2258.

10.1021/ic800709w CCC: $40.75 © 2008 American Chemical Society

Published on Web 08/09/2008

of single metal centers have served as nodes in the construction of coordination polymers.[7−12] Compared with *d*- or *f*-block ions, metal clusters generally have larger sizes and more coordination sites but smaller steric hindrance when coordinated by organic ligands, and thus some metal cluster based coordination polymers can show local connectivity numbers of eight, nine, and twelve.[7−9] In 2005, we communicated a twelve-connected coordination polymer with face-centered cubic (*fcu* in the classification of RCSR) network in which Cu_6S_4 clusters acted as nodes.[9a] In the continuing development of high-connected metal cluster based coordination polymers, we notice that the fourteen-connected body-centered cubic topology (*bcu-X* in the classification of RCSR, **sqc38** in the classification of EPINET) is well-known as the prototype of alkali metals when the six next-nearest coordination atoms are taken into consideration.[4,13] Such a fourteen-connected *bcu-X* network has not been documented in coordination polymers, although several eight-connected *bcu* networks have been reported.[6] On the basis of deduction, the design of the fourteen-connected *bcu-X* network would require a larger metal cluster as the fourteen-connected node. In this paper, we present two copper sulfur cluster based high-connected coordination polymers, namely $[Cu_3(pdt)_2(CN)]$ (**1**) and $[Cu_{19}I_4(pdt)_{12}(SH)_3]$ (**2**) (pdt = 4-pyridinethiolate). Compound **1** is a twelve-connected *fcu* topological network in which Cu_6S_4 clusters function as nodes while **2** is a fourteen-connected *bcu-X* topological network in which nanosized chiral $Cu_{19}I_4S_{12}$ clusters act as fourteen-connected nodes. It should be noted that the fourteen-connected *bcu-X* network **2** represents an undocumented topological type in coordination polymers to date. In addition to the topological importance, in situ S−C(sp^3), S−C(sp^2), and S−C(sp) cleavage reactions were observed in **1** and **2**.

Materials and Methods

All the starting materials were purchased of commercially reagent grade and used without further purification. Elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer. The Fourier transform infrared spectroscopy (FT-IR) spectra were recorded from KBr pellets in the range 400−4000 cm^{-1} on a Nicolet 5DX spectrometer. Thermogravimetric analysis (TGA) was carried out in a nitrogen or air stream using SETARAM LABSYS equipment with a heating rate of 10 °C/min. Photoluminescence analyses were performed on an Edinburgh FLS920 luminescence spectrometer.

Syntheses. $[Cu_3(pdt)_2(CN)]$ (**1**) A mixture of $Cu(MeCO_2)_2$ (0.108 g, 0.6 mmol), (4-pyridylthio)acetic acid (0.051 g, 0.3 mmol), NH_4SCN (0.018 g, 0.24 mmol), NaOH (0.015 g, 0.36 mmol), and water (7 mL) in a molar ratio of 2:1:0.8:1.2:1300 was sealed in a 15 mL Teflon-lined stainless container, which was heated to 170 °C for 120 h. After cooling to room temperature, black block crystals of **1** were recovered in 35% yield. Anal: calcd for $C_{11}H_8Cu_3N_3S_2$: C, 30.23; H, 1.85; N, 9.62. Found: C, 30.14; H, 1.90; N, 9.57. IR data (KBr, cm-1): 3419m, 3044w, 2457w, 2129m, 1684s, 1649w, 1614m, 1449w, 1402s, 1376m, 1262m, 1133s, 957m, 863m, 629m, 535s.

$[Cu_{19}I_4(pdt)_{12}(SH)_3]$ (**2**).

Method I. A mixture of $CuSO_4 \cdot 5H_2O$ (0.100 g, 0.4 mmol), pdtH (0.022 g, 0.2 mmol), KI (0.066 g, 0.4 mmol), CH_3CN (3 mL), and water (2 mL) in a mole ratio of 2:1:2:288:555 was sealed in a 15 mL Teflon-lined stainless container, which was heated to 160 °C and held 6 days. After cooling to room temperature, yellow block-like crystals of **2** were obtained in the yield of 30% (based on pdtH).

Method II. A mixture of $CuSO_4 \cdot 5H_2O$ (0.100 g, 0.4 mmol), (4-pyridylthio)acetic acid (0.035 g, 0.2 mmol), KI (0.066 g, 0.4 mmol), CH_3CN (3 mL), and water (2 mL) in a mole ratio of 2:1:2:288:555 was sealed in a 15 mL Teflon-lined stainless container, which was heated to 160 °C and held 5 days. After cooling to room temperature, yellow block-like crystals of **2** were obtained in the yield of 28%.

Method III. A mixture of CuI (0.079 g, 0.4 mmol), pdtH (0.022 g, 0.2 mmol), CH_3CN (3 mL), and water (2 mL) in a mole ratio of 2:1:288:555 was sealed in a 15 mL Teflon-lined stainless container, which was heated to 160 °C and held 5 days. After cooling to room temperature, yellow block-like crystals of **2** were obtained in the yield of 25%. Anal: calcd for $C_{60}H_{51}Cu_{19}I_4N_{12}S_{15}$: C, 22.98; H, 1.64; N, 5.36; S, 15.34. Found: C, 22.78; H, 1.71; N, 5.29; S, 15.22. IR data (KBr, cm^{-1}): 3463m, 2925w, 2361w, 2113w, 1576s, 1469m, 1409m, 1204m, 1097m, 1058w, 999m, 813m, 715m, 510s.

X-ray Crystallographic Study. Data were collected at 298 K on a Bruker Apex diffractometer (Mo Kα, $\lambda = 0.71073$ Å). Lorentz-polarization and absorption corrections were applied. The structures were solved with direct methods and refined with full-matrix least-squares technique (SHELX-97).[14] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of pdt ligands were geometrically placed and refined with isotropic temperature factors. The crystallographic data are listed in Table 1; selected bond lengths and bond angles are given in Table 2.

Results and Discussion

Description of Structures. Compound **1** crystallizes in the tetragonal non-centrosymmetrical space group $I\bar{4}2m$, and there are two crystallographically independent Cu(I) sites,

---

(8) (a) Jia, J.-H.; Lin, X.; Wilson, C.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Walker, G.; Cussen, E. J.; Schroder, M. *Chem. Commun.* **2007**, 840–842. (b) Wang, X.-L.; Qin, C.; Wang, E.-B.; Su, Z.-M.; Li, Y.-G.; Xu, L. *Angew. Chem., Int. Ed.* **2006**, *45*, 7411–7414. (c) Zhang, X.-M.; Zheng, Y.-Z.; Li, C.-R.; Zhang, W.-X.; Chen, X.-M. *Cryst. Growth Des.* **2007**, *7*, 980–983.

(9) (a) Zhang, X.-M.; Fang, R.-Q.; Wu, H.-S. *J. Am. Chem. Soc.* **2005**, *127*, 7670–7671. (b) Li, D.; Wu, T.; Zhou, X.-P.; Zhou, R.; Huang, X.-C. *Angew. Chem., Int. Ed.* **2005**, *44*, 4175–4178.

(10) (a) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469–472. (b) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982–986. (c) Livage, C.; Guillou, N.; Chaigneau, J.; Rabu, P.; Drillon, M.; Ferey, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 6488–6491. (d) Miyasaka, H.; Nakata, K.; Sugiura, K.; Yamashita, M.; Clérac, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 707–711. (e) Xiang, S.; Wu, X.; Zhang, J.; Fu, R.; Hu, S.; Zhang, X. *J. Am. Chem. Soc.* **2005**, *127*, 16352–16353.

(11) (a) Sun, D.; Ma, S.; Ke, Y.; Collins, D. J.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 3896–3897. (b) Wang, X.-S.; Ma, S.; Sun, D.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 16474–16475. (c) Ma, S.; Sun, D.; Ambrogio, M.; Fillinger, J. A.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2007**, *129*, 1858–1859.

(12) (a) Cairns, A. J.; Perman, J. A.; Wojtas, L.; Kravtsov, V. Ch.; Alkordi, M. H.; Eddaoudi, M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 1560–1561. (b) Nouar, F.; Eubank, J. F.; Bousquet, T.; Wojtas, L.; Zaworotko, M. J.; Eddaoudi, M. *J. Am. Chem. Soc.* **2008**, *130*, 1833–1835. (c) Chun, H. *J. Am. Chem. Soc.* **2008**, *130*, 800–801. (d) Lu, W.-G.; Su, C.-Y.; Lu, T.-B.; Jiang, L.; Chen, J.-M. *J. Am. Chem. Soc.* **2006**, *128*, 34–35.

(13) Delgado-Friedrichs, O.; Foster, M. D.; O'Keeffee, M.; Proserpio, D. M.; Treacy, M. M. J.; Yaghi, O. M. *J. Solid State Chem.* **2005**, *178*, 2533–2554.

(14) Sheldrick, G. M. *SHELXTL-97, Program for Crystal Structure Solution and Refinement*; University of Göttingen: Göttingen, Germany, 1997.

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

formula	$C_{11}H_8Cu_3N_3S_2$	$C_{60}H_{48}Cu_{19}I_4N_{12}S_{15}$
fw	436.94	3132.86
crystal system	Tetragonal	Cubic
space group	$I\bar{4}2m$	$I23$
a (Å)	10.2175(8)	15.9737(4)
b (Å)	10.2175(8)	15.9737(4)
c (Å)	15.4618(13)	15.9737(4)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	1614.17(19)	4075.83(18)
Z	4	2
$\rho_{calc,}$(g cm^{-3})	1.798	2.553
μ, (mm^{-1})	4.162	6.785
F(000)	856	2990
size (mm)	0.22 × 0.20 × 0.19	0.06 × 0.04 × 0.03
θ (deg)	2.39 to 27.47	1.80 to 26.98
reflections	4345/991	10441/1499
T_{max}/T_{min}	0.5052/0.4612	0.8223/0.6863
data/parameters	991/55/75	1499/0/85
S	1.044	1.121
R_1[a]	0.0370	0.0366
wR_2[b]	0.0977	0.0912
Flack factor	0.05(4)	0.07(4)
$\Delta\rho_{max}/\Delta\rho_{min}$(e A^{-3})	0.615 and −0.398	1.392 and −0.479

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Bond Lengths (Å) and Angles (deg) for **1** and **2**

compound **1**[a]			
Cu(1)−N(2a)	2.057(5)	Cu(2)−N(1)	1.876(6)
Cu(1)−N(2b)	2.057(5)	Cu(2)−S(1)	2.2434(9)
Cu(1)−S(1)	2.3053(15)	Cu(2)−S(1d)	2.2434(9)
Cu(1)−S(1c)	2.3053(15)		
N(2a)−Cu(1)−N(2b)	107.5(3)	S(1)−Cu(1)−S(1c)	108.98(8)
N(2a)−Cu(1)−S(1)	110.08(8)	N(1)−Cu(2)−S(1)	126.22(4)
N(2b)−Cu(1)−S(1)	110.08(8)	N(1)−Cu(2)−S(1d)	126.22(4)
N(2a)−Cu(1)−S(1c)	110.08(8)	S(1)−Cu(2)−S(1d)	107.55(7)
N(2b)−Cu(1)−S(1c)	110.08(8)		
compound **2**[b]			
Cu(1)−I(1a)	2.5995(8)	Cu(2)−S(1e)	2.421(2)
Cu(1)−I(1b)	2.5995(8)	Cu(2)−I(1)	2.6493(10)
Cu(1)−I(1c)	2.5995(8)	Cu(3)−S(1d)	2.277(2)
Cu(1)−I(1)	2.5995(8)	Cu(3)−S(1f)	2.277(2)
Cu(2)−N(1)	2.071(6)	Cu(3)−S(2)	2.5116(14)
Cu(2)−S(1d)	2.283(2)		
I(1a)−Cu(1)−I(1b)	109.471(1)	S(1e)−Cu(2)−I(1)	97.66(5)
I(1a)−Cu(1)−I(1c)	109.5	S(1d)−Cu(3)−S(1f)	114.47(10)
I(1b)−Cu(1)−I(1c)	109.5	S(1d)−Cu(3)−S(2)	122.77(5)
I(1a)−Cu(1)−I(1)	109.5	S(1f)−Cu(3)−S(2)	122.77(5)
I(1b)−Cu(1)−I(1)	109.5	Cu(1)−I(1)−Cu(2 g)	103.29(3)
I(1c)−Cu(1)−I(1)	109.5	Cu(1)−I(1)−Cu(2 h)	103.29(3)
N(1)−Cu(2)−S(1d)	112.98(18)	Cu(2 g)−I(1)−Cu(2 h)	114.88(2)
N(1)−Cu(2)−S(1e)	103.7(2)	Cu(1)−I(1)−Cu(2)	103.29(3)
S(1d)−Cu(2)−S(1e)	122.67(9)	Cu(2 g)−I(1)−Cu(2)	114.88(2)
N(1)−Cu(2)−I(1)	105.58(18)	Cu(2 h)−I(1)−Cu(2)	114.88(2)
S(1d)−Cu(2)−I(1)	112.14(6)		

[a] Symmetry codes: (a) $-x + 1/2, y + 1/2, -z + 1/2$; (b) $x + 1/2, -y + 1/2, -z + 1/2$; (c) $-x + 1, -y + 1, z$; (d) $-x + 1, y, -z$. [b] Symmetry codes: (a) $x, -y + 2, -z + 2$; (b) $-x, y, -z + 2$; (c) $-x, -y + 2, z$; (d) $z-1/2, -x + 3/2, -y + 3/2$; (e) $y-1/2, z + 1/2, x + 1/2$; (f) $-z + 1/2, x + 1/2, -y + 3/2$; (g) $-y + 1, z, -x + 1$; (h) $-z + 1, -x + 1, y$.

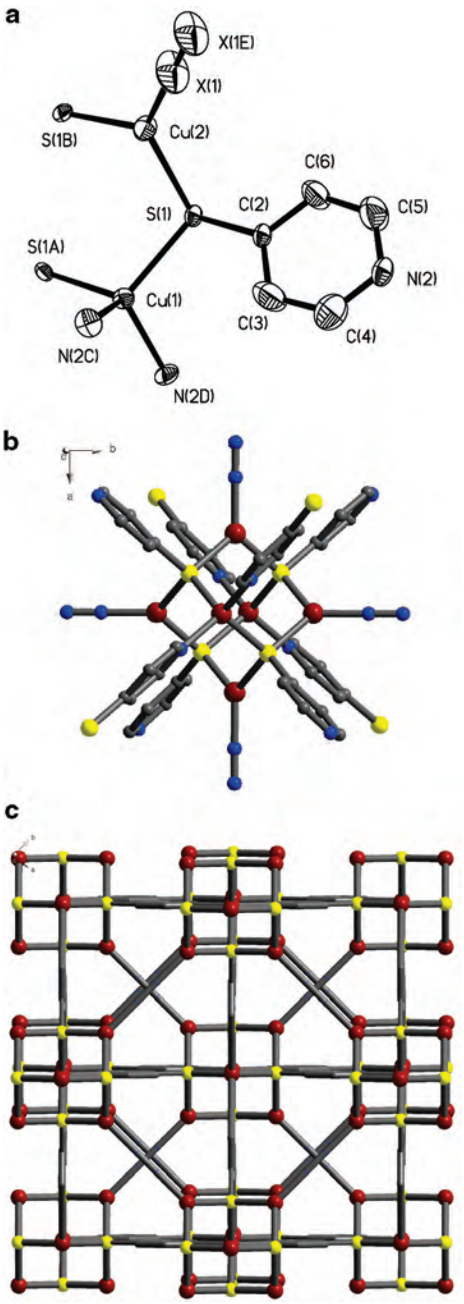


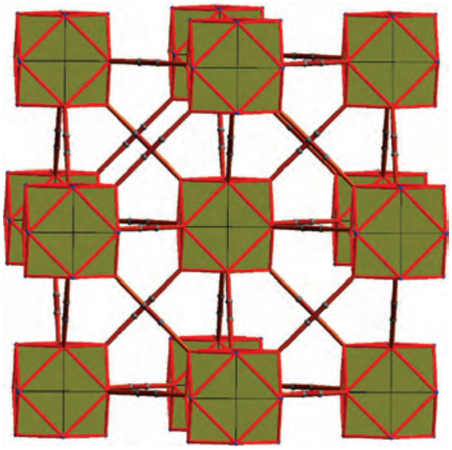
Figure 1. View of the coordination environments of copper sites (a), the twelve-connected Cu_6S_4 cluster (b), and the three-dimensional twelve-connected framework (c) in **1**.

one cyanide and one pdt (Figure 1a.) The indistinguishable C and N atoms of cyanide occupy the same sites and are labeled as X(1). The X(1)−X(1e) distance of 1.160(12) Å is typical for the cyanide group.[15] The Cu(1) site has a tetrahedral geometry and is coordinated to two S and two N atoms from four pdt ligands with Cu(1)−N distance 2.057(5) Å and Cu(1)−S distance 2.3053(15) Å. The L−Cu(1)−L (L = N, S) angles are in the range of 107.5(3)−110.08(8)°. The Cu(2) site has a trigonal geometry, coordinated to one X atom from the cyanide group and two S atoms from pdt ligands with Cu(2)−X distance 1.876(6) Å and Cu(2)−S(1) distance 2.2434(9) Å. The N−Cu(2)−S and S−Cu(2)−S angles are 126.22(4)° and 107.55(7)°, respectively. The pdt ligand coordinates to four Cu atoms in a μ_4 mode. Two Cu(2) atoms, four Cu(1) atoms, and four μ_3-S atoms form a Cu_6S_4 cluster that shows approximate T_d symmetry with six Cu(I) ions arranged into a Cu_6 octahedron and four μ_3-S atoms

---

(15) (a) Rauchfuss, T. B.; Contakes, S. M.; Hsu, S. C. N.; Reynolds, M. A.; Wilson, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 6933–6934. (b) Brousseau, L. C.; Williams, D.; Kouvetakis, J.; O'Keeffe, M. *J. Am. Chem. Soc.* **1997**, *119*, 6292–6296.

Scheme 1. Schematic View of the Augmented Twelve-Connected *fcu* Net in **1**



distributed at the centers of the trigonal faces (Figure 1b). Such a Cu_6S_4 cluster has been found in the isolated hexanuclear complex Cu_6(4-pyridinethione)$_4Cl_6$.[16] The adjacent Cu···Cu distances in the Cu_6S_4 cluster are 3.69 and 3.75 Å, which are larger than twice the van der Waals radius of copper(I) of 1.40 Å and thus eliminate the existence of cuprophilicity.[17] Each Cu_6S_4 cluster is connected to twelve adjacent Cu_6S_4 clusters via four cyanide groups and eight pyridine rings as shown in Figure 1c. The distances between the centers of the Cu_6S_4 clusters linked by pyridine rings and cyanide are 10.6 and 10.2 Å, respectively. Each Cu_6S_4 cluster has a cuboctahedral coordination figure which is enclosed by twelve adjacent Cu_6S_4 clusters. The net of **1**, when idealized, simply corresponds to a cubic closest packed array of spheres, namely, a face-centered cubic lattice as shown in Scheme 1.[18] The Schläfli symbol for the idealized net is $3^{24}\cdot4^{36}\cdot5^{6}$. It may also be described as an augmented face centered cubic lattice, and the three-letter symbol proposed by O'Keeffe is *fcu*.

Compound **2** crystallizes in the cubic chiral space group *I*23, and there are three crystallographically independent copper sites, one hydrosulfide, one iodide, and one pdt (Figure 2a.) The Cu(1) site shows an ideal tetrahedral geometry, coordinated by four equivalent iodides with Cu(1)−I(1) distance of 2.5995(8) Å and I−Cu(1)−I angle of 109.471(1)°. The Cu(2) site has a distorted tetrahedral geometry, ligated by two sulfur atoms from two pdt groups, one pyridine nitrogen, and one iodide. The Cu(2)−N(1), Cu(2)−S(1d), Cu(2)−S(1e) and Cu(2)−I(1) distances are 2.071(6), 2.283(2), 2.421(2), and 2.6493(10) Å. The L−Cu(2)−L (L =N, S, I) angles are in the range of 97.66(5)−122.67(9)°. The Cu(3) site shows a trigonal geometry, coordinated to two sulfur atoms from two pdt groups and one hydrosulfide. The Cu(3)−S distances are 2.277(2) and 2.5116(14) Å; the S−Cu(3)−S angles are 114.47(10) and 122.77(5)°. The I(1) coordinates to four Cu atoms in a μ_4 mode with Cu−I−Cu angles in the range of 103.29(3)−114.88(2)°.

The second building unit in **2** is a *T*-symmetric nanosized chiral $Cu_{19}I_4S_{12}$ cluster (Figure 2b), constructed by the $Cu_{18}S_{12}$ shell and centered CuI_4 unit. On the $Cu_{18}S_{12}$ shell (Figure 2c), six Cu(I) atoms are arranged into a Cu_6 octahedron, and the remaining twelve Cu(I) atoms are approximately located at the midpoint of twelve edges of the Cu_6 octahedron (Figure 2d). The twelve μ_3-S atoms of the $Cu_{18}S_{12}$ shell come from pdt groups and are arranged into a truncated tetrahedron (Figure 2e). The shortest Cu···Cu distances on the $Cu_{18}S_{12}$ shell are 3.57, 3.80, and 4.20 Å. The diameter of the $Cu_{19}I_4S_{12}$ cluster is beyond 1.3 nanometer after consideration of the van der Waals radii of copper(I) atoms (10.95 Å measured on the basis of diagonal copper atoms). Copper sulfur clusters generally contain even copper atoms with $Cu_{2n}S_n$ (n = 6, 12, 14, 15) cores and are centro-symmetric.[19] Different composition, odd copper atoms, chirality, and encapsulation of the CuI_4 unit make the $Cu_{19}I_4S_{12}$ cluster quite different from known sulfur-bridged copper clusters. To the best of our knowledge, the $Cu_{19}I_4S_{12}$ cluster is the only nanosized chiral sulfur-bridged copper cluster encapsulating CuI_4 unit. Each $Cu_{19}I_4S_{12}$ cluster is connected to fourteen $Cu_{19}I_4S_{12}$ clusters via twenty-four pyridine rings and six hydrosulfides to finish the fourteen-connected *bcu-X* framework (Figure 3 and Scheme 2). The nodes are nanosized chiral $Cu_{19}I_4S_{12}$ clusters, and the linkers are triple pyridine rings of pdt groups and hydrosulfides. The short Schläfli symbol is $3^{36}\cdot4^{48}\cdot5^{7}$. For an ideal *bcu-X* metal, it crystallizes in cubic centro-symmetric $Im\bar{3}m$ space group and the vertex has $m\bar{3}m$ symmetry.[4] Interestingly, replacement of the $m\bar{3}m$ symmetric vertex by a 23 symmetric $Cu_{19}I_4S_{12}$ cluster makes **2** crystallize in the cubic chiral *I*23 space group.

Synthesis Chemistry. Complexes **1** and **2** were synthesized under hydro(solvo)thermal conditions, in which some parameters such as pH value, temperature, and starting materials could influence final products. The synthesis of **1** relies on subtle control of various hydrothermal parameters, particularly starting materials, temperature, and pH value. Hydrothermal reactions of Cu(II), cyanide, and pdt ligands did not form **1**, but hydrothermal treatment of Cu(I), cyanide, and pdt ligands produced powdered **1**, indicating that slow in situ synthesis of pdt via C−S cleavage of (4-pyridylthio)-aceto is critical for growing single crystals of **1**. Besides, a similar hydrothermal reaction at a lower temperature could not produce **1**. Furthermore, the initial pH value (slightly basic, pH 8−9) is also important for the formation of **1**.

Different from **1**, the temperature plays a more important role than starting materials and pH value in the synthesis of **2**. Similar reaction at 140 °C resulted in a documented complex $[Cu_4I_4(tdp)_2]$ (tdp = 4,4′-thiodipyridine) that shows a 2-D 2-fold interpenetrated structure constructed by Cu_4I_4

---

[16] Cheng, J.-K.; Yao, Y.-G.; Zhang, J.; Li, Z.-J.; Cai, Z.-W.; Zhang, X.-Y.; Chen, Z.-N.; Chen, Y.-B.; Kang, Y.; Qin, Y.-Y.; Wen, Y.-H. *J. Am. Chem. Soc.* **2004**, *126*, 7796–7797.

[17] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

[18] (a) Friedrichs, O. D.; O'Keeffe, M.; Yaghi, O. M. *Acta Crystallogr.* **2003**, *A59*, 22–27. (b) Friedrichs, O. D.; O'Keeffe, M.; Yaghi, O. M. *Acta Crystallogr.* **2003**, *A59*, 515–525. (c) O'Keeffe, M.; Eddaoudi, M.; Li, H.; Reineke, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3–20.

[19] Dehnen, S.; Eichhöfer, A.; Corrigan, J. F.; Fenske, D. Synthesis and Characterization of IB-VI Nanoclusters. In *Nanoparticles: From Theory to Application*; Günter, Schmid, Ed.; Wiley-VCH-Verlag GmbH & Co. KgaA: Weinheim, 2004; Chapter 3, p 107.

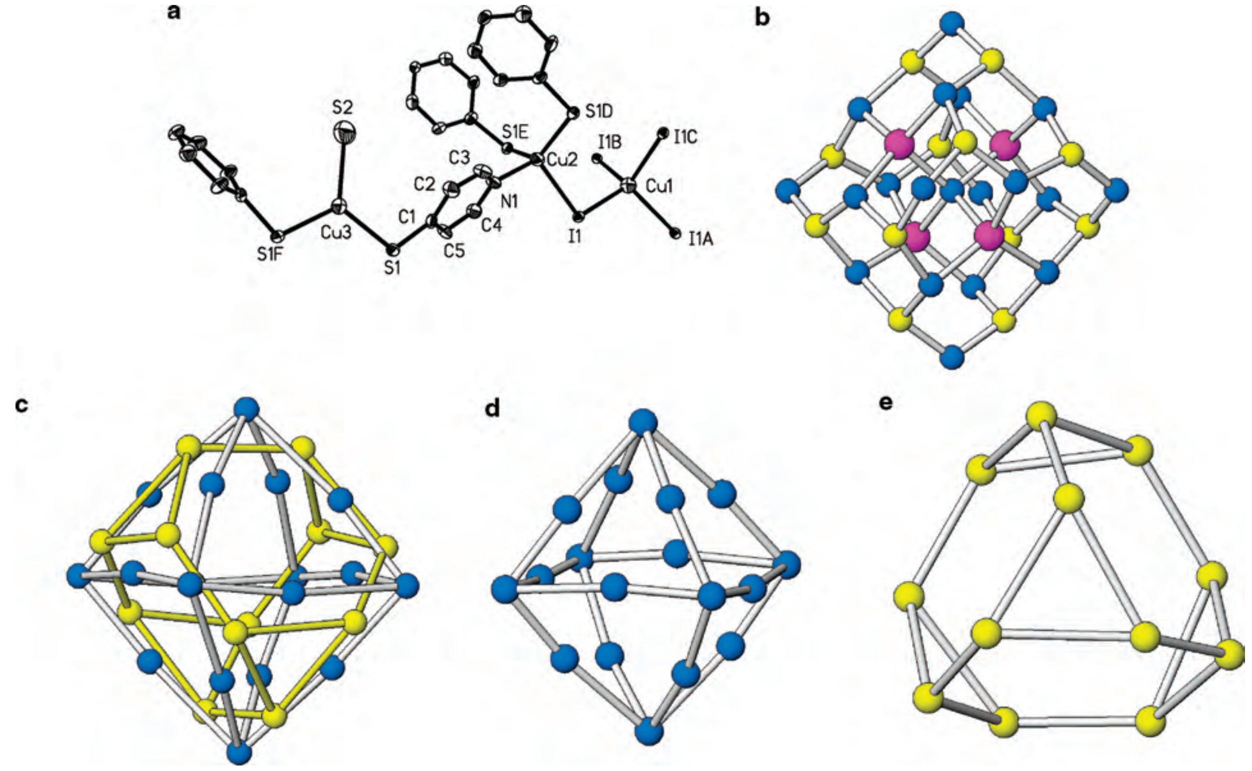


Figure 2. View of the coordination environments of Cu sites in **2** (a), the chiral *T*-symmetric $Cu_{19}I_4S_{12}$ cluster (b), the $Cu_{18}S_{12}$ shell showing octahedral Cu_{18} and truncated tetrahedral S_{12} cages (c), the Cu_{18} cage (d), and the S_{12} cage (e) in the $Cu_{19}I_4S_{12}$ cluster. The Cu, I, and S atoms are shown in blue, purple, and yellow color, respectively. The S−S and Cu−Cu linkages do not represent bonding interactions.

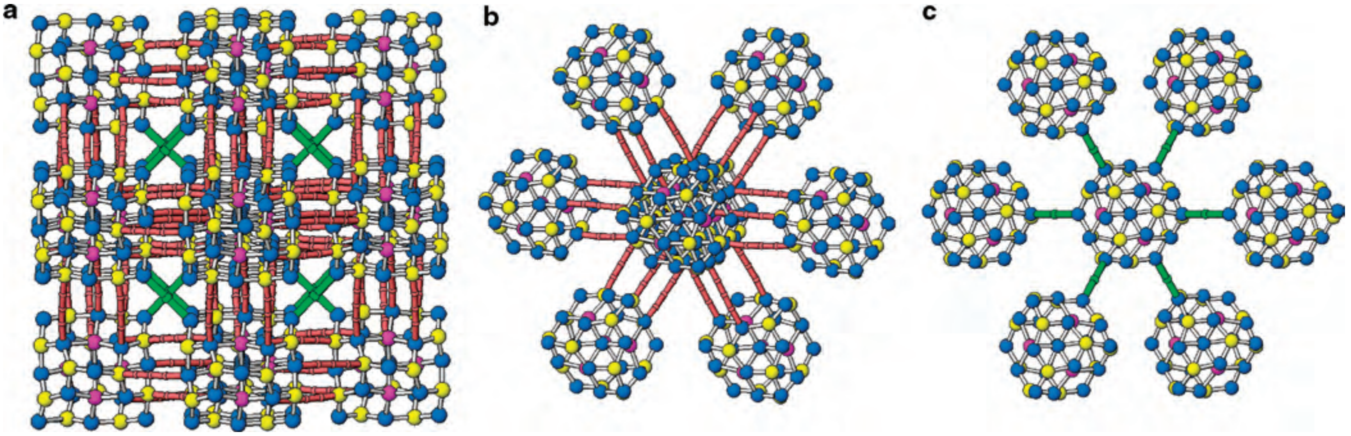


Figure 3. (a) View of the fourteen-connected body-centered cubic framework constructed by $Cu_{19}I_4S_{12}$ clusters. For clarification, hydrosulfides and pyridine rings of pdt groups are represented by green and red rods, respectively. (b) View one $Cu_{19}I_4S_{12}$ cluster linking eight $Cu_{19}I_4S_{12}$ clusters via twenty-four pyridine rings. For clarification, red rods represent pyridine rings of pdt groups. Note that three $Cu_{19}I_4S_{12}$ clusters are overlapped and every three pyridine rings act as one connector. (c) View one $Cu_{19}I_4S_{12}$ cluster linking six $Cu_{19}I_4S_{12}$ clusters via six hydrosulfides. For clarification, green rods represent hydrosulfides.

cubane units.[20] When reaction temperature was further lowered to 120 °C, a polymorph of [Cu_4I_4(tdp)$_2$] with a 2-D sheet structure was obtained.[21] To note, **2** can be available by similar solvothermal treatment of three different mixtures (Mixture I: $CuSO_4$, pdtH, and KI; Mixture II: $CuSO_4$, (4-pyridylthio)acetic acid, and KI; Mixture III: CuI and pdtH) in aqueous acetonitrile solution at 160 °C. In situ ligand synthesis has been incorporated to prepare novel coordination complexes from metal ions and organic precursors in the crystal engineering of coordination complexes.[22] The presence of pdt and cyanide in **1** indicates in situ S−C(sp^3) cleavage of (4-pyridylthio)acetate and S−C(sp) cleavage of thiocyanate. A drop of of Ba(NO_3)$_2$ solution was added to the filtrate, and a white precipitation appeared immediately, indicating the existence of sulfate anions in the filtrate and allowing us to speculate that the sulfur of thiocyanate was

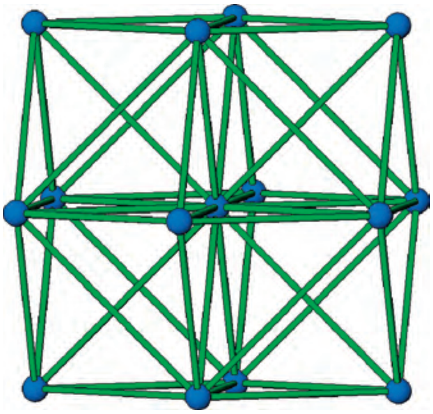
---

(20) Wang, J.; Zheng, S.-L.; Hu, S.; Zhang, Y.-H.; Tong, M.-L. *Inorg. Chem.* **2007**, *46*, 795–800.

(21) Crystal data for [Cu_4I_4(tdp)$_2$]: monoclinic, $P2_1/m$, $M_r = 569.12$, $a = 11.5166(17)$ Å, $b = 4.9102(6)$ Å, $c = 19.489(3)$ Å, $\beta = 107.034(3)°$, $V = 899.2(2)$ Å^3, $Z = 2$, $D_c = 2.102$ g cm^{-3}, $\mu = 5.896$ mm^{-1}, $T_{min} = 0.4924$, $T_{max} = 0.8429$, $F(000) = 524$, $R_1 = 0.0702$, w$R_2 = 0.1931$, $S = 1.162$.

(22) (a) Chen, X.-M.; Tong, M.-L. *Acc. Chem. Res.* **2007**, *40*, 162–170. (b) Zhang, X.-M. *Coord. Chem. Rev.* **2005**, *249*, 1201–1219.

Scheme 2. Schematic View of the Fourteen-Connected *bcu-X* Net in **2**

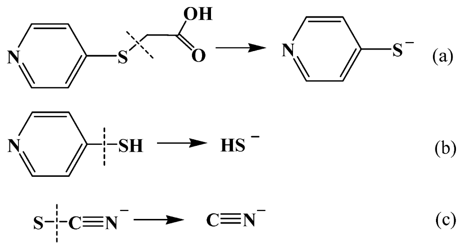


oxidized into sulfates in the preparation of **1**. The formation of cyanide by oxidized S−C(sp) cleavage of thiocyanate was initially documented by Schug and co-workers, and their studies also revealed that sulfur of SCN^- was converted to sulfate.[23] Recently, this kind of S−C(sp) cleavage of thiocyanate has been used to prepare CuCN based coordination polymers.[24] The in situ S−C(sp^3) cleavage of (4-pyridylthio)acetate to form pdtH has also been observed in compounds $[Ln_2(C_2O_4)_3(pdtH)_2(H_2O)_2]_n$.[25] Besides, pdtH can also form via solvothermal in situ disulfide cleavage reactions.[26]

There are three methods for **2** and particularly SO_4^{2-} groups are absent in Method III. Thus, it is believed that hydrosulfide in **2** came from S−C cleavage of pdt or (4-pyridylthio)-acetic acid. The reduction of sulfate in Methods I and II into hydrosulfide can be eliminated. The partial decomposition of pdt groups via S−C(sp^2) cleavage has been observed, and the resulting hydrosulfide is generally oxidized into sulfate.[16,20] Hydrothermal in situ ligand reactions involving pdtH are complicated and interesting, and sometimes pdtH groups can be converted into 4,4′-dipyridylsulfide via in situ desulfation coupling.[27] Three types of S−C cleavage reactions observed in **1** and **2** are shown in Scheme 3.

Thermogravimetry and Photoluminescence. The TGA trace of **1** (Figure 4a) in air at the heating rate of 10 °C min^{-1} shows that **1** is thermally stable up to 205 °C in air. A slight weight increase and subsequent mass loss (4.8%) in the range of 210−350 °C indicates addition of oxygen and removal of cyanide. The decomposition of the pdt groups starts at 430 °C and is not finished up to 700 °C. TGA for **2** was conducted in nitrogen atmosphere at the heating rate of 10 °C min^{-1}. As shown in Figure 4b, almost no weight loss occurred until 250 °C, indicating good thermal stability of **2**. The stable residue is not formed up to 700 °C.

Scheme 3. Schematic View of Three Types of S−C Cleavage Reactions in **1** and **2**



Complex **1** does not display remarkable photoluminescent properties at ambient temperature similar to the isolated hexanuclear complex Cu_6(4-pyridinethione)$_4Cl_6$.[16] However, in solid state and at ambient temperature, **2** shows an intense yellow emission at 574 nm (182.7 ns) and a much weaker blue emission at 466 nm (1.6 ns) upon photoexcitation at 350nm (Figure 5). In general, possible assignments for the excited states responsible for emission phenomena of Cu(I)-complexes are ligand centered $\pi \rightarrow \pi^*$ transitions (LC), ligand-to-ligand (LLCT), ligand-to-metal (LMCT), or metal-to-ligand (MLCT) charge transfer transitions or metal centered $d^{10} \rightarrow d^9s^1$ (MC) transitions. According to decay lifetimes and related copper(I) thiolate/iodide clusters, the blue emission is tentatively assigned as an intraligand $\pi \rightarrow \pi^*$ transition while the yellow emission is assigned to originate from a mixture of LMCT (S,I→Cu) and copper-centered d→s,p character.[28]

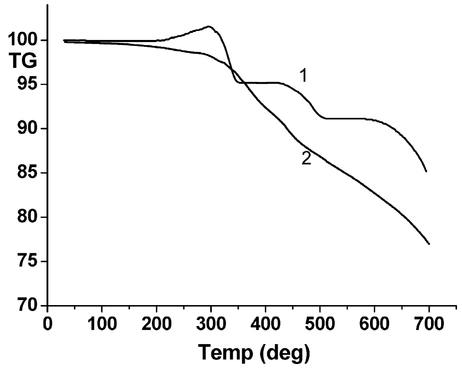


Figure 4. TGA curves of **1** in air (a) and **2** in a nitrogen stream (b) at the heating rate of 10 °C per min.

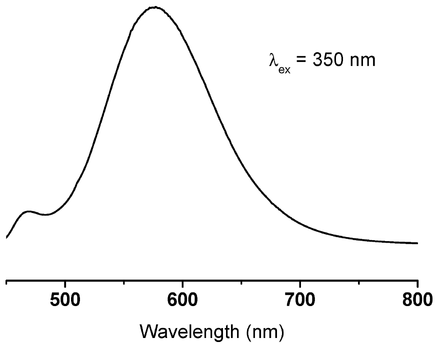


Figure 5. Photoluminescent emissions of **2** upon excitation at 340 nm.

---

(23) (a) Schug, K.; Gilmore, M. D.; Olson, L. A. *Inorg. Chem.* **1967**, *6*, 2180–2185. (b) Schug, K.; Miniatas, B.; Sadowski, A. J.; Yano, T.; Ueno, K. *Inorg. Chem.* **1968**, *7*, 1669–1670.

(24) Zhou, X.-P.; Li, D.; Wu, T.; Zhang, X.-J. *Dalton Trans.* **2006**, 2435–2443.

(25) He, Y.-K.; Han, Z.-B.; Ma, Y.; Zhang, X.-D. *Inorg. Chem. Commun.* **2007**, *10*, 829–832.

(26) Wang, J.; Zhang, Y.-H.; Li, H.-X.; Lin, Z.-J.; Tong, M.-L. *Cryst. Growth Des.* **2007**, *7*, 2352–2360.

(27) Hao, Z.-M.; Zhang, X.-M. *Cryst. Growth Des.* **2007**, *7*, 64–68.

(28) (a) Yam, V. W.-W.; Lo, K. K.-W. *Chem. Soc. Rev.* **1999**, *28*, 323–334. (b) Ford, P. C.; Cariati, E.; Bourassa, J. *Chem. Rev.* **1999**, *99*, 3625–3647.

Conclusion

Hydro(solvo)thermal reactions generated twelve-connected face-centered cubic (*fcu*) and fourteen-connected body-centered cubic (*bcu-X*) coordination polymers. The Cu_6S_4 and the nanosized chiral $Cu_{19}I_4S_{12}$ clusters have been used as nodes in the two high-connected coordination polymers, and in situ S−C bond cleavage reactions have been observed. This work further demonstrates that the replacement of *d*- or *f*-block ions with metal clusters as nodes is a feasible route to synthesize high-connected metal-organic frameworks.

Acknowledgment. This work was financially supported by NSFC (20771069), FANEDD (200422) and Fok Ying Tung Education Foundation (111015) and Nature Science Foundation of Shanxi (200801107).

Supporting Information Available: Crystal structural data for **1** and **2** in CIF format. This material is available free of charge via http://pubs.acs.org.

IC800709W