DOI: 10.1002/ejic.200900559

# Two New Helical Compounds Based on Pitch-Tunable Keggin Clusters

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**Keywords:** Polyoxometalates / Helical structures / Luminescence / Electrochemistry

Two isostructural compounds, $\{[Cu_2(DF)_2H_2O]_2SiW_{12}O_{40}\}\cdot 2H_2O$ (**1**) and $\{[Cu_2(DF)_2H_2O]_2GeMo_{12}O_{40}\}\cdot 2H_2O$ (**2**) (DF = 4,5-diazafluoren-9-one), were synthesized and characterized by routine methods and single-crystal X-ray diffraction. In the compounds, each Keggin cluster links five copper dimers $[Cu_2(DF)_2H_2O]^{2+}$ in an unusual asymmetrical pentacoordination mode to form 3D networks with left- and right-handed helical chains. Notably, by comparing **1** and **2** with other helical compounds with Keggin clusters as connectors, we found that the pitches of those compounds are mainly dominated by the coordination modes of the Keggin clusters, suggesting that the Keggin clusters are pitch-tunable synthons. Furthermore, the luminescent and electrochemical properties of the title compound were studied.

## Introduction

Helical structures, the foundation of the genetic code, have become a topic of intense interest in coordination and materials chemistry in recent years. Many chemists have put great efforts on the rational design and synthesis of artificial helical compounds,[1] which show significance in multidisciplinary areas such as biology, optical devices, and asymmetric catalysis.[2a–2d] The first inorganic double helix self-assembled from simple starting materials under hydrothermally conditions was reported by Haushalter and Zubieta et al.[2e]

Polyoxometalates (POMs),[3–7] as a large family of metal–oxygen clusters, constitute a fascinating class of inorganic systems that is incomparable in structural diversity as well as in a wide range of applications.[8–15] Helical compounds based on POMs have attracted more and more attention because of their attractive structural features and potential applications, and many such compounds have been successfully synthesized.[16–20] The roles of POMs in those artificial helical structures can be divided into three kinds: (i) POMs act as templates enraptured in the helical network;[16a] (ii) POMs are pendants attached in the helical chains;[16b–16e,17d,20f] (iii) POMs are connectors of the helical chains. For the third kind, a series of POM-based compounds was isolated, including vanadates,[1d,17a–17c,20e] Anderson-type POMs,[18] isopolymolybdates,[19] and so on,[20a–20d] whereas those involving Keggin POMs are rare.[16f,16g] Note that the Keggin POMs, having a number of coordinating O atoms (12 terminal and 24 $\mu_2$-O atoms), can offer smart sites to link metal centers or metal complex units, and their globular surface makes their coordination sites more flexible to adjust steric hindrance.

Recently, Hong et al. pointed out that the use of twisted rigid ligands as structure-directing agents is an effective approach to obtain helical structures with ease.[2c] The Keggin clusters are reminiscent of twisted rigid ligands, as they can provide globular coordination environment and twisted binding sites, thus having the makings of pitch-tunable connectors to construct helical compounds.

In our previous work,[21] we isolated a compound containing a copper dimer subunit with a hinge motif, $[Cu_2(DF)_2H_2O]^{2+}$ (DF = 4,5-diazafluoren-9-one) (Supporting Information, Scheme S1), which makes it a potential linkage to synergically tune the helical structure in the Keggin cluster-based helical assembly.

On the basis of these considerations, we chose a copper–DF complex and a Keggin POM in an attempt to construct helical compounds. Fortunately, we obtained two new compounds, $\{[Cu_2(DF)_2H_2O]_2SiW_{12}O_{40}\}\cdot 2H_2O$ (**1**) and $\{[Cu_2(DF)_2H_2O]_2GeMo_{12}O_{40}\}\cdot 2H_2O$ (**2**), which are isostructural, possessing the left- and right-handed helical chains. The structural features of the two compounds verify the pitch tunableness of the Keggin POMs.

## Results and Discussion

Compounds **1** and **2** were synthesized under identical hydrothermal conditions. All W and Mo atoms are in the +VI oxidation state obtained by bond valence sum (BVS) calculations and XPS (Supporting Information, Figure S1).[22] The copper atoms in compounds **1** and **2** are all in the +I

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.200900559.

oxidation state, confirmed by their coordination environments, BVS calculations,[22] crystal color, and XPS (Supporting Information, Figures S1 and S2). The oxidation state of the Cu center changed from +II to +I, and such a phenomenon is often observed in hydrothermal reaction systems containing both N-donor organic ligands and $Cu^{II}$ ions.[23]

## Structural Description

X-ray single-crystal diffraction analysis revealed that compounds **1** and **2** are isostructural; therefore, we will discuss the structure of **1** as an example in detail. Compound **1** consists of three basic subunits with two kinds of motifs: two copper dimers $[Cu_2(DF)_2H_2O]^{2+}$ with a hinge motif ($Cu_2$-**A** and $Cu_2$-**A′**) and one Keggin cluster $[SiW_{12}O_{40}]^{4-}$ (**B**) with a global motif (Figure 1).

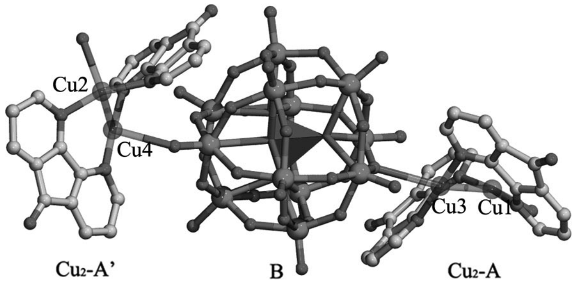

Figure 1. Combined polyhedral–ball-and-stick representation of the fundamental units in compounds **1**. All hydrogen atoms are omitted for clarity.

There are four crystallographically independent Cu atoms with two coordination modes. Cu1, Cu2, and Cu4 are tetracoordinated in a tetrahedral geometry achieved by two nitrogen atoms of two DF molecules and two oxygen atoms from one $SiW_{12}$ cluster and one $H_2O$ molecule for Cu1 and Cu4, and from two $SiW_{12}$ clusters for Cu2, respectively. Cu3 is tricoordinated in a "T"-type geometry achieved by two nitrogen atoms of two DF molecules and one oxygen atom of a $SiW_{12}$ cluster. By these coordination modes, Cu1 and Cu3 form the $Cu_2$-**A** dimer and Cu2 and Cu4 form the $Cu_2$-**A′** dimer, respectively (Supporting Information, Figure S3). The bond lengths around the Cu atoms are in the ranges 2.300–2.808 Å (Cu–O) and 1.881–1.997 Å (Cu–N), and the O–Cu–O angles are in the range 75.901–101.164°; N–Cu–N angles are between 159.26 and 175.45°. Remarkably, in the dimers, the two adjacent Cu···Cu distances (Cu1···Cu3 2.551 Å and Cu2···Cu4 2.553 Å) are much shorter than the van der Waals contact distance (2.8 Å) of copper, indicating a strong metal–metal bond between the two Cu centers, comparable with the compounds reported.[24] Given these Cu–Cu bonds, Cu1 is in a trigonal bipyramidal geometry ($\tau$ = 0.866), and Cu2 and Cu4 are both in a rectangular pyramidal geometry ($\tau$ = 0.200 for Cu2 and $\tau$ = 0.150 for Cu4).[25] Additionally, Cu3 is tetracoordinated in a tetrahedron geometry. The $SiW_{12}$ anion exhibits a classical α-Keggin configuration.[26] Interestingly, the $SiW_{12}$ cluster, as a pentadentate inorganic ligand, provides one bridging O atom bonding to Cu3 and other four terminal O atoms bonding to four Cu atoms (one Cu1, two Cu2, and one Cu4; Supporting Information, Figure S4). To the best of our knowledge, this coordination pattern not only exhibits an unusual asymmetrical coordination mode[27] but also presents a rare example of a pentadentate ligand for Keggin POMs.

Another structural feature for **1** is the helical chains, which can be described as follows: Each $Cu_2$-**A′** dimer links two $SiW_{12}$ clusters through a Cu2 atom and each $SiW_{12}$ cluster links two Cu2 atoms through its two terminal O atoms (O16 and O9) with ca. 120° of the angle O16–Si–O9. Consequently, the $Cu_2$-**A′** dimer and the $SiW_{12}$ cluster are connected alternately through Cu–O bonds, forming the left- and right-handed helical chains along the crystallo-

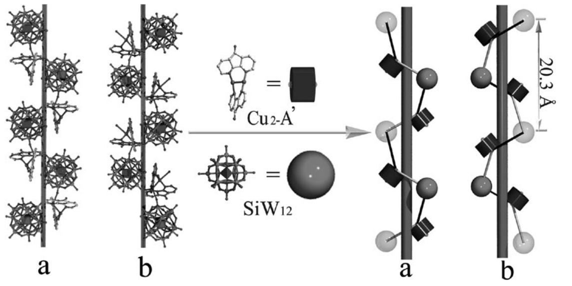

Figure 2. Diagram of the left- (a) and right-handed (b) helical chains in **1**.

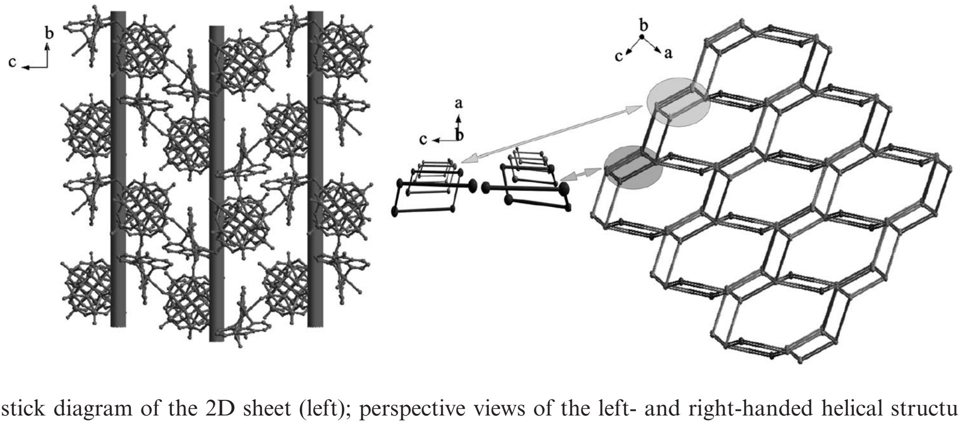

Figure 3. Ball-and-stick diagram of the 2D sheet (left); perspective views of the left- and right-handed helical structures along the chain directions (middle); schematic view of the $(4^2 8^1 10^1 12^6)(4^1 10^1 12^1)$ topology (right) in compound **1**.

graphic $2_1$ screw axis in the [010] direction with a pitch of 20.3 Å (Figure 2). In the chain, multiple H-bonds exist between the $SiW_{12}$ clusters and the DF molecules, which may stabilize the helical chains (Supporting Information, Figure S5). Furthermore, adjacent helical chains are linked together through Cu4 atoms of the $Cu_2$-**A′** dimers to form a sheet (Figure 3, left). Then, these 2D sheets are extended by $Cu_2$-**A** dimers to form a unique 3D network. Topological analysis of the structure was performed by considering each $SiW_{12}$ cluster as a five-connected node, each $Cu_2$-**A** dimer as a two-connected node, and each $Cu_2$-**A′** dimer as a three-connected node, which can be symbolized as a network with a $(4^2 8^1 10^1 12^6)(4^1 10^1 12^1)$ topology (the first symbol for $SiW_{12}$ cluster; the second for $Cu_2$-**A′** dimer; Figure 3, right). To the best of our knowledge, this kind of network has never been described so far in POM chemistry.

### The Pitch Tunableness of the Keggin POMs

We mentioned above that several helical compounds in which the Keggin clusters act as connectors were isolated. When determining the structures of the representative helical compounds, $(Et_3NH)_2[Cu^I_2(Hfcz)_2(SiW_{12}O_{40})]\cdot 2H_2O$ (**a**),[16f] $[Na(H_2O)_3(H_2L)SiW_{12}O_{40}](H_2L)_2$ (**b**),[16g] $\{[Cu_2(DF)_2H_2O]_2SiW_{12}O_{40}\}$ (**c** = **1**), and $(Et_3NH)_2[Cu^I_2(Hfcz)_2(SiW_{12}O_{40})]\cdot H_2O$ (**d**),[16f] we found that the Keggin clusters adopted three coordination modes in these helical chains: (i) one terminal O and one bridging O atoms, $\angle\alpha \approx 31°$; (ii) two terminal O atoms, $\angle\alpha \approx 120°$; (iii) two bridging O atoms, $\angle\alpha \approx 180°$ ($\angle\alpha$ is defined as the angle formed by two lines from the center of the Keggin cluster to the two oxygen atoms that are the connected sites of helical chain). Figure 4 is the chart of the pitches versus $\angle\alpha$ for the four compounds, which shows that the pitches of the helical chains increase with an increase in $\angle\alpha$. It is notable that in these compounds the helical chains are made of Keggin POMs and other subunits, but no matter what the other subunits are, the pitch has an approximately linear relation with $\angle\alpha$. It is also notable that for compounds b and c, their $\angle\alpha$ are the same, whereas the pitches are slightly different perhaps due to various subunits other than the Keggin clusters (Supporting Information, Figure S6). These facts suggest that the pitches of the helical compounds are mainly dominated by the coordination modes of the Keggin clusters.

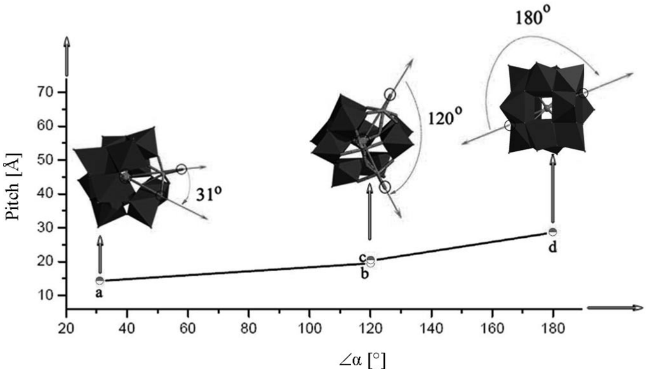

Figure 4. Chart of the pitch vs. $\angle\alpha$ for compounds **a**–**d**.

### FTIR Spectra

As shown in Figure S7 (Supporting Information), the IR spectra exhibit the characteristic peaks of an α-Keggin structure at 963, 913, 881, and 786 cm$^{-1}$ in **1**; 984, 942, 892, and 772 cm$^{-1}$ in **2**, which are attributed to $\nu(X–O_c)$, $\nu(M=O_t)$, $\nu_{as}(M–O_b–M)$, and $\nu_{as}(M–O_c–M)$ (X = Si, M = W for **1**; X = Ge, M = Mo for **2**), respectively. In addition, bands in the 1103–1730 cm$^{-1}$ region can be assigned to characteristic peaks of the DF molecules.

### XRPD Patterns

The XRPD patterns for **1** and **2** are presented in Figure S8 (Supporting Information). The diffraction peaks of both simulated and experimental patterns match well, indicating the phase purities of these two compounds.

### Thermal Study

The TG curves of compounds **1** and **2** are provided in Figure S9 (Supporting Information). The TG curves of both compounds exhibit a similar two-step weight loss. The first weight loss step corresponds to the loss of water molecules, 1.76% (calcd. 1.83%) in the range 15–260 °C for **1** and 2.52% (calcd. 2.47%) in the range 33–270 °C for **2**. The second weight loss step is ascribed to the loss of organic molecules DF, 18.68% (calcd. 18.55%) in the range 260–571 °C for **1** and 25.51% (calcd. 26.49%) in the range 260–560 °C for **2**.

### Cyclic Voltammetry (CV)

To study the redox properties of compounds **1** and **2**, the carbon paste electrodes (CPEs; **1**-CPE and **2**-CPE) were prepared. The electrochemical behaviors were studied in 1 M $H_2SO_4$ solution at a scan rate of 60 mV s$^{-1}$. For **1**-CPE, as shown in Figure S10 (1a; Supporting Information), in the potential range +300 to –600 mV, there exist two quasireversible redox waves with half-wave potentials $E_{1/2} = (E_{pa} + E_{pc})/2$, –357 mV (II–II′), and –510 mV (III–III′), and one irreversible anodic wave (I) at 126 mV. The irreversible anodic wave (I) is assigned to the oxidation of $Cu^I$.[28a] The II–II′ and III–III′ redox waves can be attributed to the reductive process of $W^{VI}$. In comparison with the electrochemical behaviors of the parent $SiW_{12}$ anion in acidic solution reported in the literature,[28b] there exist two differences: first, the reversibility is decreased in **1**-CPE; secondly, only two pairs of redox waves are observed and the third pair of redox waves of the two-electron reductive processes in the parent anion $SiW_{12}$ disappears in the same potential range for **1**-CPE. This phenomenon is also observed in the similar copper/$SiW_{12}$ compound.[28c] However, **2**-CPE has a similar redox waves to those of the $PMo_{12}$ anion in acidic solution reported in the literature,[28b] as shown in Figure S10 (2a; Supporting Information), in the potential range +600 to –200 mV. There exist three quasireversible redox waves with half-wave potentials $E_{1/2} = (E_{pa} + E_{pc})/2$, 358 mV (I–I′), 251 mV (II–II′), and 36 mV (III–III′). The three redox waves correspond to the three consecutive two-electron reductive processes of $Mo^{VI}$.[28a] However, the oxidation peak of the copper centers is not observed in the scan range +600 to –200 mV. This phenomenon is also observed in the similar Mo/Cu systems.[28b] For both CPEs, as shown in Figure S10 (Supporting Information), when the scan rates are varied from 60 to 220 $mV\,s^{-1}$, the peak potentials change gradually: the cathodic peak potentials shifted to the negative direction and the corresponding anodic peak potentials to the positive direction. When the scan rates are lower than 120 $mV\,s^{-1}$, the peak currents are proportional to the scan rates, which indicates that the redox processes are surface-controlled, and the exchanging rate of electrons is fast; however, when the scan rates were higher than 120 $mV\,s^{-1}$, the peak currents are proportional to the square root of the scan rate, which indicates that the redox processes of the CPEs are diffusion-controlled.[28d]

### Luminescence Properties

The presence of direct metal–metal interactions may be one of the important factors contributing to the luminescent properties of coinage $d^{10}$ metal coordination compounds. Therefore, the luminescent properties of compounds **1** and **2** were also studied in the solid state at room temperature (Figure 5). Compounds **1** and **2** display deep-blue emission bands at ca. 443 and 429 nm, respectively, upon excitation at 245 nm. As is known, the mono-$Cu^I$–phen complexes (phen = 1,10-phenanthroline) have no luminescent properties,[29] the mono-$Cu^I$–DF complexes should be the same, as the DF molecule is similar to the phen molecule. So in our case, the emissions are tentatively assigned to interdimer Cu···Cu interactions.[30] Because compounds **1** and **2** are thermally stable and insoluble in common polar and nonpolar solvents, they may be good candidates for potential solid-state luminescent materials.

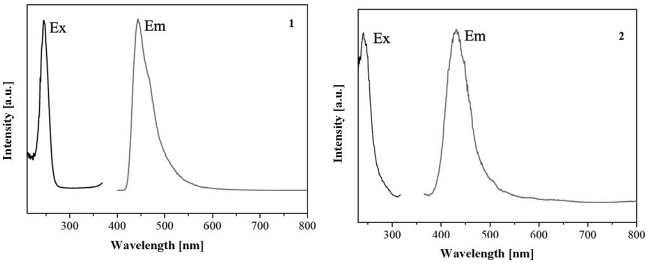

Figure 5. Luminescent spectra of **1** and **2** in the solid state at room temperature. Ex = excitation, Em = emission.

## Conclusions

In this paper, two new compounds, possessing the left- and right-handed helical chains with Keggin clusters as connectors, were synthesized under hydrothermal conditions. The structural features of the two compounds verify the pitch tunableness of the Keggin POMs. This fact, to some extent, provides a calculable clue for the design and synthesis of new helical compounds based on Keggin POMs. The luminescent properties of the two compounds show a potential application in blue emission materials.

## Experimental Section

**Materials and General Procedures:** All reagents were purchased commercially and used without further purification. Organic ligand DF was synthesized in the laboratory[31] and confirmed by $^1H$ NMR and IR spectroscopy. Elemental analyses (C, H, and N) were performed with a Perkin–Elmer 2400 CHN Elemental Analyzer. The IR spectra were obtained with an Alpha Centaurt FTIR spectrometer with KBr pellets in the 400–4000 $cm^{-1}$ region. The thermogravimetric (TG) analyses were carried out with a Perkin–Elmer TGA7 instrument in flowing $N_2$ with a heating rate of 10 $°C\,min^{-1}$. Cyclic voltammograms (CVs) were obtained with a CHI 660 electrochemical workstation at room temperature. Platinum gauze was used as a counter electrode and Ag/AgCl electrode was referenced. Chemically bulk-modified carbon paste electrodes (CPEs) were used as working electrodes. The XRPD patterns were obtained with a Rigaku D/ma × 2500V PC diffractometer with Cu-$K_\alpha$ radiation, the scanning rate was $4°s^{-1}$, $2\theta$ ranging from 4–40°. Luminescence measurements were carried out with a Hitachi F-4500 Fluorescence Spectrophotometer.

**$\{[Cu_2(DF)_2H_2O]_2SiW_{12}O_{40}\}\cdot 2H_2O$ (1):** In a typical experiment, a mixture of $H_4[SiW_{12}O_{40}]\cdot 14H_2O$ (340 mg, 0.1 mmol), $Cu(CH_3COO)_2\cdot 2H_2O$ (149 mg, 0.8 mmol), DF (36 mg, 0.2 mmol), and $H_2O$ (10 mL) was stirred for 1 h. The pH was adjusted to 4.6 with 1 M NaOH, and then the mixture was transferred to an 18-mL Teflon-lined reactor and kept under autogenous pressure at 160 °C for 4 d. After the reactor had slowly cooled to room temperature over a period of 10 $°C\,h^{-1}$, dark-red crystals of **1** were obtained. The dark-red crystals were picked out, washed with distilled water, and dried at room temperature (51% yield based on W). $C_{44}H_{32}Cu_4N_8O_{48}SiW_{12}$ (3929.08): calcd. C 13.45, H 0.82, N 2.85; found C 13.52, H 0.73, N 2.92.

**$\{[Cu_2(DF)_2H_2O]_2GeMo_{12}O_{40}\}\cdot H_2O$ (2):** The preparation of compound **2** was similar to that of **1**, except that $H_4[GeMo_{12}O_{40}]\cdot 13H_2O$ (206 mg, 0.1 mmol) was used instead of $H_4[SiW_{12}O_{40}]\cdot 14H_2O$. The dark-red crystals were picked out, washed with distilled water, and dried at room temperature (42% yield based on Mo). $C_{44}H_{32}Cu_4GeMo_{12}N_8O_{48}$ (2918.8): calcd. C 18.10, H 1.10, N 3.83; found C 18.26, H 1.02, N 3.92.

**Preparation of 1-CPE and 2-CPE:** Graphite powder (48 mg) and **1** (8 mg) were mixed and ground together with an agate mortar and pestle to achieve a uniform mixture. Then nujol (0.6 mL) was added with stirring. The homogenized mixture was packed into a glass tube with a 1.2 mm inner diameter, and the tube surface was wiped with paper. Electrical contact was established with a copper rod through the back of the electrode. In a similar manner, **2**-CPE was made from compound **2**.

**X-ray Crystallographic Study:** The data were collected with a Bruker Smart Apex CCD diffractometer with Mo-$K_\alpha$ ($\lambda$ =

0.71073 Å) at 273 K by using the $\omega$-scan technique. Empirical absorption correction was applied. The structures of **1** and **2** were solved by direct methods and refined by full-matrix least-squares analysis on $F^2$ by using the SHELXTL-97 software.[32] Compound **1** was refined with two equally weighted $SiW_{12}$ anions, with one rotating by ca. 90° and superimposing on the other one.[33] Some oxygen atoms of **2** are disordered with two possible positions and the occupancies refined to 50%. The organic hydrogen atoms were generated geometrically. The crystal data and structure refinements of **1** and **2** are summarized in Table 1. CCDC-727549 (for **1**) and -727550 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Selected crystallographic data for **1** and **2**.[a,b]

| | **1** | **2** |
|---|---|---|
| Formula | $C_{44}H_{32}N_8O_{48}Cu_4SiW_{12}$ | $C_{44}H_{32}N_8O_{48}Cu_4GeMo_{12}$ |
| $M_r$ | 3929.08 | 2918.80 |
| Color, habit | dark red, block | dark red, block |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ |
| $a$ [Å] | 13.456(5) | 13.398(5) |
| $b$ [Å] | 20.317(5) | 20.385(5) |
| $c$ [Å] | 25.347(5) | 25.414(5) |
| $\beta$ [°] | 90.806(5) | 90.496(5) |
| $V$ [Å$^3$] | 6929(3) | 6941(3) |
| $Z$ | 4 | 4 |
| $D_{calcd}$ [g cm$^{-3}$] | 3.760 | 2.786 |
| $F$(000) | 6984.0 | 5520.0 |
| Refl. measured | 40220 | 29518 |
| Refl. unique | 10017 | 9848 |
| $R_{int}$ | 0.1095 | 0.0299 |
| $R_1/wR_2$ [$I>2\sigma(I)$] | 0.0870,0.2030 | 0.0876, 0.1749 |
| GoF ($F^2$) | 1.112 | 1.146 |

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

**Supporting Information** (see footnote on the first page of this article): XPS of **1** and **2**; optical photo pictures of **1** and **2**; process of formation of the Cu dimer; connecting modes of the two copper dimers; coordination mode of the $SiW_{12}$ cluster; representative H-bonds in the helical chain; helical structure for compounds **b** and **c**; IR spectra of **1** and **2**; simulated and experimental PXRD for **1** and **2**; TG curves of **1** and **2**; CVs of **1**-CPE and **2**-CPE.

## Acknowledgments

This work is financially supported by the National Natural Science Foundation of China (20671016), the Program for Changjiang Scholars and Innovative Research Team in University, and the Analysis and Testing Foundation of Northeast Normal University.

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Received: June 20, 2009