



# Effect of the Keggin anions on assembly of Cu<sup>I</sup>-bis(tetrazole) thioether complexes containing multinuclear Cu<sup>I</sup>-cluster

Xiu-Li Wang\*, Qiang Gao, Ai-Xiang Tian, Hai-Liang Hu, Guo-Cheng Liu

Department of Chemistry, Bohai University, Liaoning Province Silicon Materials Engineering Technology Research Centre, Jinzhou 121000, PR China

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## ABSTRACT

In order to investigate the effect of polyoxometalate (POM) on the assembly of transition metal-bis(tetrazole) thioether complexes, three new complexes based on different Keggin anions and multinuclear Cu<sup>I</sup>-cluster [Cu<sub>12</sub>(bmtr)<sub>9</sub>(HSiMo<sub>12</sub>O<sub>40</sub>)<sub>4</sub>] (**1**), [Cu<sub>3</sub>(bmtr)<sub>3</sub>(PM<sub>12</sub>O<sub>40</sub>)] (*M*=W for **2**; Mo for **3**) (bmtr=1,3-bis(1-methyl-5-mercapto-1,2,3,4-tetrazole)propane), have been hydrothermally synthesized and characterized by routine physical methods and single crystal X-ray diffraction. In compound **1**, two kinds of nanometer-scale tetranuclear subunits linked by [SiMo<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> polyanions assemble a (3, 4)-connected three-dimensional (3D) self-penetrating framework. Compounds **2** and **3** are isostructural, exhibiting a 1D chain with [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup>/[PMo<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> polyanions and trinuclear clusters arranging alternately. The distinct structural differences between these POM-based Cu<sup>I</sup>-bmtr complexes of **1** and **2/3** maybe rest on the contrast of Keggin-type polyoxometalate with different central heteroatoms, which have been discussed in detail. In addition, the electrochemical properties of the title complexes have been investigated.

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## 1. Introduction

Polyoxometalates (POMs), as a unique class of discrete-molecular metal-oxo clusters, possess various structural versatility [1], multiple coordination sites and abundant properties, such as electrochemical activity, magnetic, photochemical and catalytic properties [2]. At present, introducing the transition metal-organic complexes into POM field to assemble POM-based functional materials has attracted more attention [3]. A large amount of new POM-based compounds of this series with zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) frameworks have been reported [4,5]. Recently, the flexible organic ligands, such as flexible bis-pyridyl, bis-imidazol and bis-triazole type ligands, have received more extensive concern, which can combine the transition metal ions together modifying POMs [6]. In this work, we select a flexible 1,3-bis(1-methyl-5-mercapto-1,2,3,4-tetrazole) propane (bmtr) (Chart 1) to modify POMs. Compared with the classical flexible organic ligands mentioned above, the bis-(tetrazole) thioether ligands exhibit more advantages in the construction of POMs-based compounds: First, it has more potential coordination sites, such as six N and two S donors, which can strengthen its coordination ability accordingly. Second, three adjacent N donors

in one tetrazole group may induce to form multinuclear transition metal clusters with ease. Third, the introduction of S atoms further promotes the molecular flexibility obviously, which can be viewed as the unique feature of these bis-(tetrazole) thioether ligands [7].

Up to now, considerable effort has been devoted to explore the synthetic rules under hydrothermal conditions for obtaining novel POM-based complexes [8]. However, many reaction factors can influence the self-assembly processes, such as nature of metal ions and ligands, mole ratio of reactants, reaction temperature, time, pH, and so on [9]. So it is still a challenging but meaningful area. In our previous work, a series of POM-based transition metal-bis(tetrazole) thioether complexes have been successfully obtained, and the influences of spacer length of organic ligands and transition metal coordination nature on assembly of these POM-based compounds have been systematically discussed, respectively [10]. In order to systematically explore the effect of Keggin polyanions on transition metal-bis(tetrazole) thioether complexes, in this work, we choose Keggin anions [SiMo<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> and [PM<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> (*M*=Mo and W), which possess different central heteroatoms, to assemble with copper ions and bmtr ligand. Fortunately, three POM-based Cu<sup>I</sup>-bmtr coordination polymers, [Cu<sub>12</sub>(bmtr)<sub>9</sub>(HSiMo<sub>12</sub>O<sub>40</sub>)<sub>4</sub>] (**1**), [Cu<sub>3</sub>(bmtr)<sub>3</sub>(PM<sub>12</sub>O<sub>40</sub>)] (*M*=W for **2**; Mo for **3**) were obtained under the same conditions. Interestingly, compound **1** exhibits an unusual 3D self-penetrating framework with [SiMo<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> polyanion, while compounds **2** and **3** are isostructural, showing an absolutely different 1D

\* Corresponding author. Tel.: +86 416 3400158.

E-mail address: wangxiuli@bhu.edu.cn (X.-L. Wang).

chain structure with the  $[\text{PM}_{12}\text{O}_{40}]^{3-}$  ( $M=\text{W}$  for **2**;  $\text{Mo}$  for **3**) polyanions. The Keggin polyanions with different central heteroatoms play a key role in assembly of these compounds.

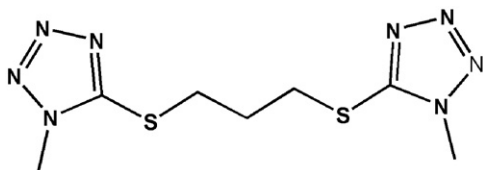
## 2. Experimental

### 2.1. Materials and general methods

All reagents were purchased commercially and used without further purification. The organic ligand bmtr was prepared according to the literature method [11]. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra (KBr pellets) were recorded on a Magna FT-IR 560 spectrometer. Thermogravimetric analyses (TGA) were carried out on a Pyris Diamond instrument in flowing  $\text{N}_2$  with a heating rate of  $10^\circ\text{C min}^{-1}$ . A CHI 440 electrochemical workstation connected to a Digital-586 personal computer was used for the control of the electrochemical measurement and data collection. A conventional three-electrode system was used. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum wire as the counter electrode. The title compounds chemically bulk-modified carbon-paste electrodes (CPEs) were used as the working electrodes.

### 2.2. Synthesis of $[\text{Cu}_3^{II}(\text{bmtr})_3(\text{HSiMo}_{12}\text{O}_{40})_4]$ (**1**)

$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (0.12 g, 0.60 mmol),  $\text{H}_4\text{SiMo}_{12}\text{O}_{40} \cdot 26\text{H}_2\text{O}$  (0.16 g, 0.07 mmol) and bmtr (0.054 g, 0.20 mmol) were dissolved in 10 mL of distilled water. The pH of the mixture was adjusted with 1 M HCl solution to about 3 and then sealed into a 20 mL Teflon-lined autoclave. After heating for 3 day at  $160^\circ\text{C}$ , the reactor was slowly cooled to room temperature. Blocklike orange crystals of **1** were obtained in 43% yield (based on Mo). Elemental analysis (%) calcd for  $\text{Cu}_{12}\text{C}_{63}\text{S}_{18}\text{N}_{72}\text{H}_{112}\text{Si}_4\text{Mo}_{48}\text{O}_{160}$ : C 2.56, H 1.12, N 10.08; found C 2.60, H 1.13, N 10.00. IR data (KBr pellet,



**Chart 1.** Schematic representation of 1,3-bis(1-methyl-5-mercapto-1,2,3,4-tetrazole) propane (bmtr).

**Table 1**

The crystal and structure refinement data for compounds **1–3**.

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	$\text{C}_{63}\text{H}_{109}\text{Cu}_{12}\text{N}_{72}\text{O}_{160}\text{Si}_4\text{S}_{18}\text{Mo}_{48}$	$\text{C}_{21}\text{H}_{36}\text{Cu}_3\text{N}_{24}\text{O}_{40}\text{PS}_6\text{W}_{12}$	$\text{C}_{21}\text{H}_{36}\text{Cu}_3\text{N}_{24}\text{O}_{40}\text{PS}_6\text{Mo}_{12}$
Formula weight	10,492.25	3884.84	2830.02
Temperature (K)	296(2)	296(2)	296(2)
Crystal system	Trigonal	Monoclinic	Monoclinic
Space group	$R\bar{3}$	$C2/c$	$C2/c$
$a$ (Å)	18.8445	18.888(3)	18.853(2)
$b$ (Å)	22.6331	22.612(3)	22.631(2)
$c$ (Å)	16.1757	16.303(3)	16.1982(16)
$\alpha$ ( $^\circ$ )	90	90	90
$\beta$ ( $^\circ$ )	95.701(2)	95.871(3)	95.732(2)
$\gamma$ ( $^\circ$ )	90	90	90
$Z$	6	4	4
$D$ (calcd), $\text{g m}^{-3}$	2.593	3.720	2.739
$V$ ( $\text{Å}^3$ )	40,312(8)	6926.4(19)	6876.6(12)
$R_1, wR_2$ (all data)	0.0756, 0.1581	0.0665, 0.0709	0.0508, 0.1054

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

$\text{cm}^{-1}$ ): 3400(s) 1620(m), 1426(m), 833(s), 886(s), 710(m), 580(w).

### 2.3. Synthesis of $[\text{Cu}_3^I(\text{bmtr})_3(\text{PW}_{12}\text{O}_{40})]$ (**2**)

Compound **2** was prepared in a manner similar to that for **1**, but the polyoxometalate  $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 26\text{H}_2\text{O}$  (0.20 g, 0.07 mmol) was used instead of  $\text{H}_4\text{SiMo}_{12}\text{O}_{40} \cdot 26\text{H}_2\text{O}$ . Red block crystals of **2** were obtained in 36% yield (based on W). Elemental analysis (%) calcd for  $\text{Cu}_3\text{C}_{21}\text{H}_{36}\text{N}_{24}\text{S}_6\text{O}_{40}\text{PW}_{12}$ : C 6.48, H 0.93, N 8.64; found C 6.43, H 0.97, N 8.62. IR data (KBr pellet,  $\text{cm}^{-1}$ ): 2355(m), 1985(w), 1458(m), 1185(s), 1074(s), 990(s), 899(s), 801(s).

### 2.4. Synthesis of $[\text{Cu}_3^I(\text{bmtr})_3(\text{PMo}_{12}\text{O}_{40})]$ (**3**)

Compound **3** was prepared in a manner similar to that for **1**, but the  $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$  (0.15 g, 0.07 mmol) was used instead of  $\text{H}_4\text{SiMo}_{12}\text{O}_{40} \cdot 26\text{H}_2\text{O}$ . Rufous block crystals of **3** were obtained in 40% yield (base on Mo). Elemental analysis (%) calcd for  $\text{Cu}_3\text{C}_{21}\text{H}_{36}\text{N}_{24}\text{S}_6\text{O}_{40}\text{PMo}_{12}$ : C 8.90, H 1.27, N 11.87; found C 8.85, H 1.30, N 11.85. IR data (KBr pellet,  $\text{cm}^{-1}$ ): 1933(m), 1608(m), 1458(s), 1179(s), 964(s), 860(s), 717(s), 568(s).

### 2.5. Preparation of 1-, 2- and 3-CPEs

The compound **1** bulk-modified CPE (**1-CPE**) was fabricated as follows: 0.03 g of compound **1** and 0.5 g of graphite powder were mixed and grounded together by an agate mortar and pestle to achieve a uniform mixture, and then 0.18 mL of Nujol was added with stirring. The homogenized mixture was packed into a glass tube with a 3 mm inner diameter, and the tube surface was wiped with weighing paper. Electrical contact was established with a copper rod through the back of the electrode. In a similar manner, **2-** and **3-CPEs** were made with compounds **2** and **3**, respectively.

### 2.6. X-ray crystallographic study

The crystal data for title compounds were collected on a Bruker Smart 1000 CCD diffractometer with  $\text{Mo } K_\alpha$  radiation ( $\lambda=0.71069 \text{ \AA}$ ) by  $\omega$  and  $\theta$  scan mode at room temperature. The structures were solved by direct methods and refined on  $F^2$  by full-matrix least squares using the SHELXL package [12]. All of the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms on carbon atoms were calculated theoretically. The C11 atom in compound **2** and the C8 atom in **3** are crystallographically disordered into two symmetrical positions with

each carbon site half-occupied. The crystal data and structure refinements for the title compounds are summarized in Table 1. Selected bond distances and angles for the three compounds are listed in Table S1 (supporting information). The CCDC reference numbers are 832, 844, 846 for the title compounds.

### 3. Result and discussion

#### 3.1. Structure description

Single crystal X-ray analysis shows that the asymmetric unit of **1** possesses two crystallographically independent  $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$  anions (abbreviated as  $\text{SiMo}_{12}$ ), four crystallographically independent  $\text{Cu}^{\text{I}}$  ions and three bmtr ligands (Fig. 1). The valence sum calculations [13] show that all the Cu atoms are in +I oxidation state and all the Mo atoms are in +VI oxidation state. To balance the charge of compound **1**, a proton is added [14]. In compound **1**, there exist two kinds of tetranuclear  $\text{Cu}^{\text{I}}$ -clusters ( $M_1$ ,  $M_2$ ), which are formed by four  $\text{Cu}^{\text{I}}$  ions and four bmtr ligands, respectively (Fig. S1). The difference between  $M_1$  and  $M_2$  rests on their liganacy to  $\text{SiMo}_{12}$ . In  $M_1$  subunit, both Cu1 and Cu3 atoms coordinate with the oxygen atoms from  $\text{SiMo}_{12}$ ; while in  $M_2$  subunit, only Cu4 atoms coordinate with the oxygen atoms of  $\text{SiMo}_{12}$ . Each of the bmtr ligands shows the 3 and 4 position nitrogen atoms coordination mode. Two kinds of steric conformation of bmtr, U-type and line-type, can be found in compound **1** (Fig. S2).

As shown in Fig. 2, these two kinds of tetranuclear subunits  $M_1$  and  $M_2$  arrange alternately by sharing the same linear bmtr ligands to form a 1D chain. Furthermore, the  $\text{SiMo}_{12}$  polyanions show two different kinds of coordination modes in **1** (Fig. S3). The  $\text{SiMo}_{12}^{4-}$  is

six-coordinated by three pairs of Cu1 and Cu3 ions through O58 and O59 atoms, which can be viewed as a 3-connected node to connect with three  $M_1$  subunits. Meanwhile, the  $\text{SiMo}_{12}^{4-}$  is single coordinated by the Cu4 ion from  $M_2$ . The  $M_1$  subunits connect adjacent  $\text{SiMo}_{12}^{4-}$  polyanions to form a 2D hexagon network based on 12-membered rings, in which the 12-membered ring formed by six  $\text{SiMo}_{12}^{4-}$  polyanions and six  $M_1$  subunits shows a chair-shaped configuration (Fig. 3). These 2D networks are linked by  $M_2$  and further extended into a 3D framework. The angles around Cu ion are  $97.8(3)$ – $141.8(5)^\circ$  for N–Cu–N,  $90.6(3)$ – $108.9(3)^\circ$  for N–Cu–O and the bond lengths are  $1.941(7)$ – $2.084(8)$  Å for Cu–N,  $2.300(6)$  Å for Cu–O. Considering the  $\text{SiMo}_{12}^{4-}$  and the  $M_1$  as 3- and 4-connected nodes, respectively, we can obtain a  $(3, 4)$ -connected 3D framework with a  $(8^3)_2(8^5 \cdot 12)_3$  topology, as shown in Fig. 4. It is worth noting that there exists a self-penetrating feature in this 3D topology (Figure S4). To our knowledge, it is very rare that multinuclear subunits are extended into a high dimensional framework by covalent bonds in coordination chemistry.

Crystal structure analyses reveal that compounds **2** and **3** are isostructural, and compound **2** has been taken as an example to describe their crystal structures. As shown in Fig. 5, compound **2** consists of three  $\text{Cu}^{\text{I}}$  ions, three bmtr ligands and one  $\text{PW}_{12}$  polyanion. The valence sum calculations [13] show that all the W atoms are in the +VI oxidation state and all the Cu atoms are in the +I oxidation state.

In compound **2**, there are two crystallographically independent copper ions (Cu1 and Cu2). The Cu1 ion is four-coordinated

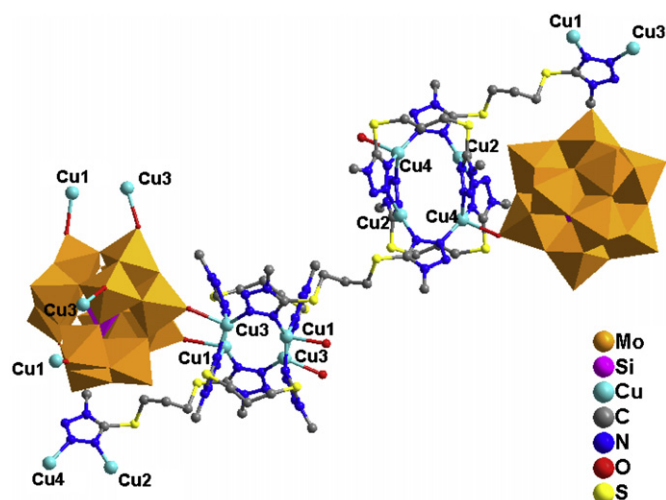


Fig. 1. Ball-stick polyhedral view of the molecule structure of **1**. The hydrogen atoms are omitted for clarity.

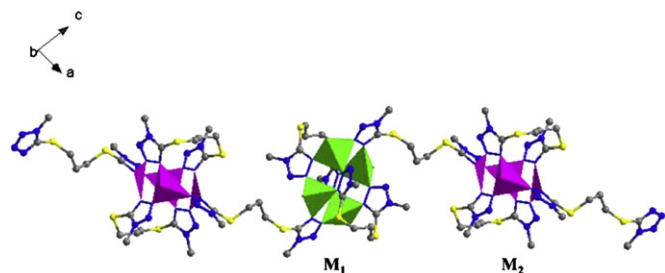


Fig. 2. The chain structure formed by  $M_1$  (green) and  $M_2$  (purple) subunits in compound **1**.

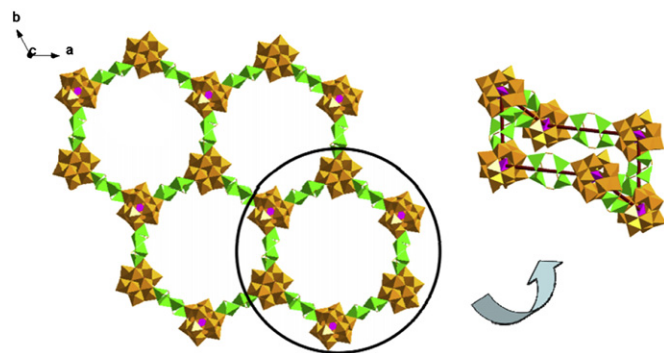


Fig. 3. The 2D network and chair-shaped configuration of the 12-membered ring in compound **1**.

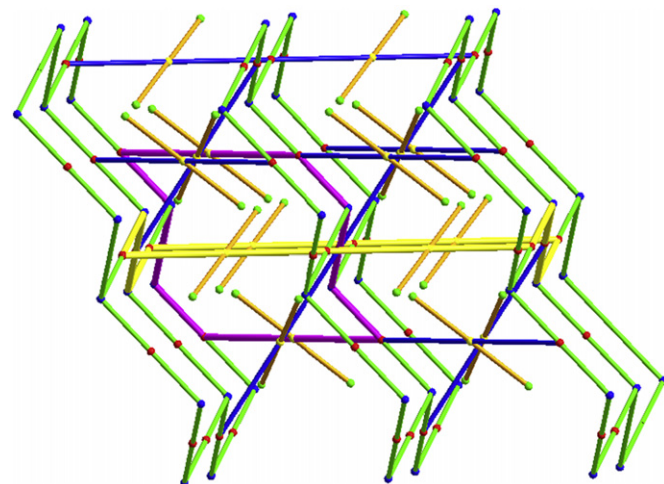


Fig. 4. Schematic representation of the 3D framework of compound **1**, where the blue balls are  $\text{SiMo}_{12}^{4-}$ , the green balls are  $\text{SiMo}_{12}^{4-}$ , the red balls are  $M_1$  and the yellow balls are  $M_2$ .

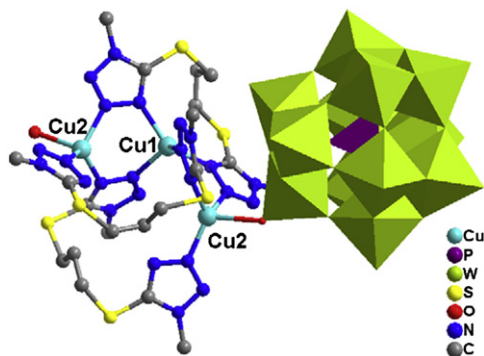


Fig. 5. Ball-stick polyhedral view of the molecule structure of **2**. The hydrogen atoms are omitted for clarity.

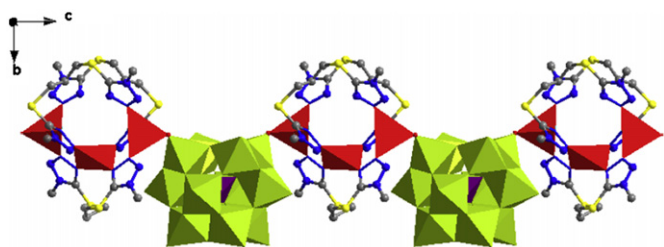


Fig. 6. The 1D chain in **2** with the  $PW_{12}$  anions and trinuclear clusters arranging alternately.

by four N atoms from three bmttr ligands in a ‘seesaw’ style. The bond distances and angles around the Cu1 are 2.066(10) and 2.075(11) Å for Cu–N and 97.9(4)–142.8(6)° for N–Cu–N. The Cu2 ion is also four-coordinated by three N atoms from three bmttr ligands and one terminal O atom from one  $PW_{12}$  anion. The bond distances and angles around the Cu2 ions are 1.947(11)–2.029(11) Å for Cu–N, 2.342(9) Å for Cu–O, 103.5(4)–124.7(4)° for N–Cu–N and 98.1(4) and 89.4(4)° for N–Cu–O. These bond distances and angles are comparable to those in the four-coordinated  $Cu^I$  compounds [6].

In compound **2**, the bmttr ligand exhibits two coordination styles: (i) It acts as a tridentate linkage, using one N atom from one tetrazole group and two N atoms from the other tetrazole group to coordinate with three  $Cu^I$  ions in unusual asymmetrical coordination mode (Fig. S5a); (ii) It provides four N donors to link three  $Cu^I$  ions, in which two N12 atoms from two tetrazole groups chelate one  $Cu^I$  ion and the left two N4 donors link two  $Cu^I$  ions, respectively (Fig. S5b). Thus, the N4-containing bmttr ligand acts as not only a bridging ligand, but also a chelate one. The bmttr in compound **2** shows a single U-shaped steric conformation. Furthermore, the  $S(CH_2)_3S$  spacer exhibits its flexibility and conformational freedom as expected.

In compound **2**, three  $Cu^I$  ions are assembled by three bmttr ligands to form a trinuclear metal-organic subunit. The  $PW_{12}$  poly-anion, as a bidentate inorganic linkage, provides two terminal O13 atoms to connect adjacent trinuclear metal-organic subunits. Thus, a 1D chain is formed with trinuclear subunits and  $PW_{12}$  poly-anions arranging alternately (Fig. 6). Interestingly, two adjacent 1D chains interlace to form a zipper-like structure (Fig. S6). The molecule structure and 1D chain of compound **3** are presented in Fig. S7.

### 3.2. Effect of different Keggin anions on assembly of this series of complexes

In our previous work, a novel (3, 4)-connected 3D self-penetrating POM-based metal-organic framework (MOF),  $[Cu_{12}(C_7H_{12}N_8S_2)_9]$

$(HSiW_{12}O_{40})_4 \cdot 0.5H_2O$  (**CC-1**), has been obtained by using Cu ions, bmttr ligands and  $SiW_{12}$  poly-anions [7]. The net of **CC-1** was considered as the first high-dimensional MOF combining two

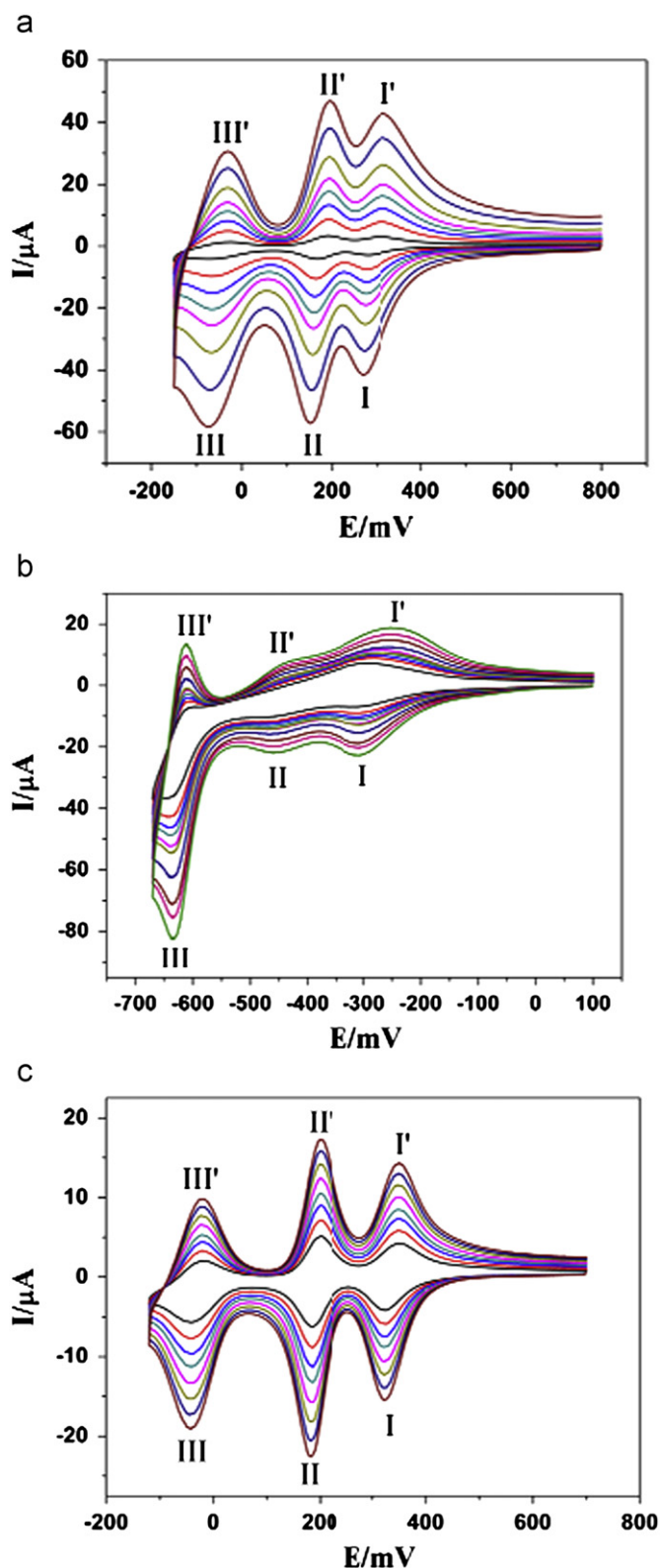


Fig. 7. (a) Cyclic voltammograms of the 1-CPE in 1 M  $H_2SO_4$  aqueous solution at different scan rates (from inner to outer: 80, 120, 140, 160, 180, 200, 250, 300  $mV s^{-1}$ ); (b) Cyclic voltammograms of the 2-CPE in 1 M  $H_2SO_4$  aqueous solution at different scan rates (from inner to outer: 60, 80, 120, 160, 200, 250, 300, 400, 500 and 600  $mV s^{-1}$ ); (c) Cyclic voltammograms of the 3-CPE in 1 M  $H_2SO_4$  aqueous solution at different scan rates (from inner to outer: 60, 80, 120, 160, 200, 250, 300, 400  $mV s^{-1}$ ).

subunits: POMs and metallacalixarenes. In order to explore whether the polyanions have influences on the structural assembly, we try to use other Keggin anions, such as the similar  $\text{SiMo}_{12}$  and different

$\text{PMo}_{12}$  and  $\text{PW}_{12}$  polyanions, to assemble with copper ions and bmt ligand under the similar condition. First, the similar  $\text{SiMo}_{12}$  polyanion was selected instead of  $\text{SiW}_{12}$  and a crystallographically isostructural compound (**1**) has been obtained. Second, we choose the different Keggin anion  $\text{PW}_{12}$ , which owns different central heteroatom P, different sizes and negative charge. Then, an absolutely different 1D chain structure was formed. Thus, the different Keggin anions really have effect on assembly of these structures. Third, in order to further prove this viewpoint, the  $\text{PMo}_{12}$  polyanion with similarity to  $\text{PW}_{12}$  was chosen. Fortunately, an isostructural compound **3** with **2** has been obtained as expected. In a word, compounds **CC-1** and **1** constructed by  $\text{SiM}_{12}$  ( $M=W$  for **CC-1**, Mo for **1**) show the same 3D structures through using the same type of Keggin polyanions, while compounds **2** and **3** constructed by  $\text{PM}_{12}$  ( $M=W$  for **2**, Mo for **3**) are also isostructural 1D chain. In addition, when  $\text{SiM}_{12}$  was used, the tetranuclear  $\text{Cu}^{\text{I}}$ -clusters were formed in **CC-1** and **1**, when  $\text{PM}_{12}$  was employed, the trinuclear  $\text{Cu}^{\text{I}}$ -clusters were obtained in **2** and **3**. The results reveal that Keggin polyanions with different central atoms show great effect on the assembly of this series.

### 3.3. Electrochemical property

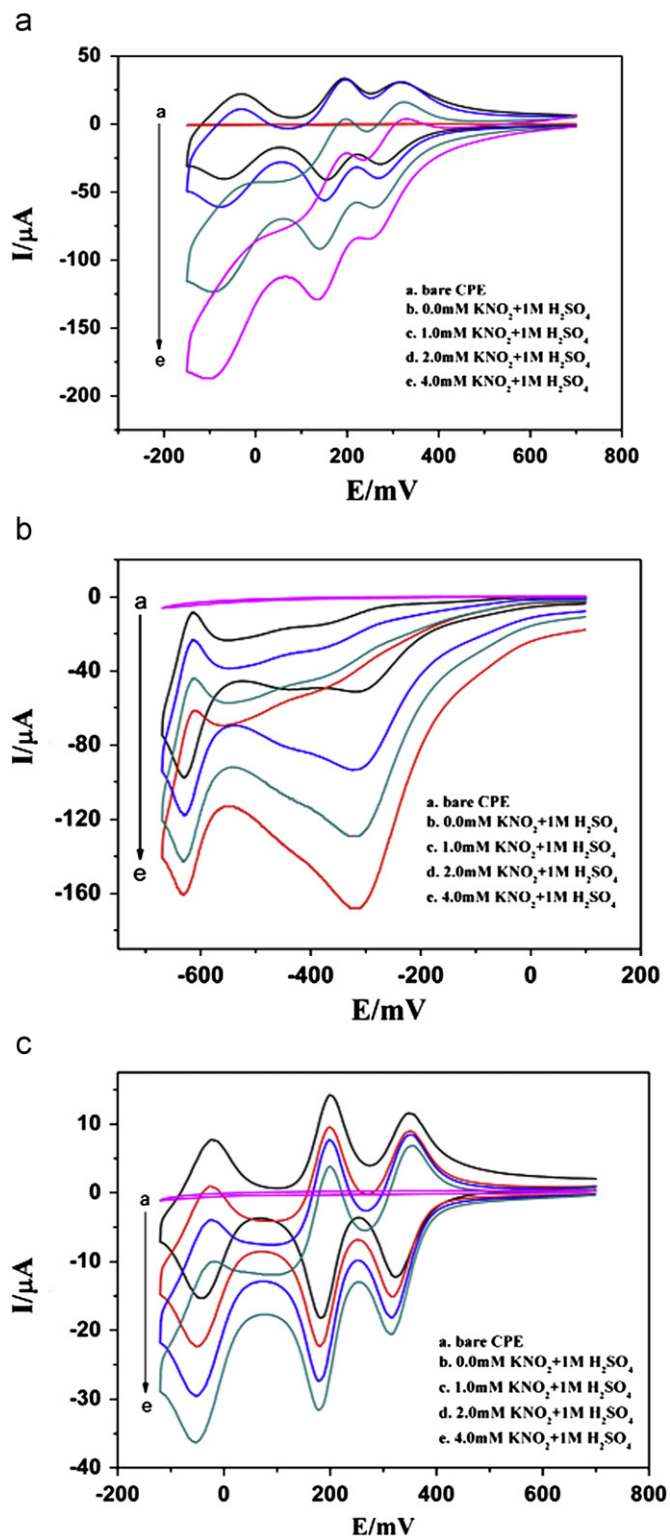
The cyclic voltammograms for **1**-, **2**- and **3**-CPEs in the 1 M  $\text{H}_2\text{SO}_4$  aqueous solution at different scan rates are presented in Fig. 7. It can be seen clearly that three reversible redox peaks (I-I', II-II', III-III') appear in the potential range from +800 to -150 mV for **1**-CPE. The mean peak potentials  $E_{1/2}=(E_{pc}+E_{pa})/2$  are 293, 170, -55 mV (scan rate:  $200 \text{ mV s}^{-1}$ ), which can be attributed to the redox of  $\text{SiMo}_{12}$  polyanions [15]. In the potential range of +100 to -670 mV for **2**-CPE, there are three pairs of quasi-reversible redox peaks I-I', II-II' and III-III' with the mean peak potentials  $E_{1/2}=(E_{pc}+E_{pa})/2$  of -289, -440, -623 mV (scan rate:  $200 \text{ mV s}^{-1}$ ), attributable to the redox of  $\text{PW}_{12}$  polyanions [16]. In the potential range of +700 to -120 mV for **3**-CPE, there are also three pairs of reversible redox peaks I-I', II-II' and III-III' with the mean peak potentials  $E_{1/2}=(E_{pc}+E_{pa})/2$  of 337, 191, -33 mV (scan rate:  $200 \text{ mV s}^{-1}$ ), attributable to the redox of  $\text{PMo}_{12}$  polyanions [17]. When the scan rates increased, the cathodic peak currents and the corresponding anodic peak currents increased simultaneously, which are proportional to scan rates (Fig. S8), suggesting that the redox processes of **1**-, **2**- and **3**-CPEs are surface-controlled.

As is known, direct electroreduction of nitrite requires a large overpotential at most electrode surfaces [18]. Therefore no obvious response is observed at a bare CPE. However, the **1**-, **2**- and **3**-CPEs display good electrocatalytic activity toward the reduction of nitrite in 1 M  $\text{H}_2\text{SO}_4$  aqueous solution in the potential range from +800 to -160 mV for **1**-CPE, +100 to -670 mV for **2**-CPE and +700 to -120 mV for **3**-CPE. As shown in Fig. 8, with the addition of nitrite, all the reduction peak currents increase markedly while the corresponding oxidation peak currents decrease, suggesting that the reduction of nitrite is mediated by the reduced species of  $\text{SiMo}_{12}$  polyanions in compound **1**,  $\text{PW}_{12}$  polyanions in compound **2** and  $\text{PMo}_{12}$  polyanions in compound **3**. The dependence curves of reduction peak currents III on concentration of nitrite are presented in Fig. S9.

Notably, the isostructural compounds **2** and **3** exhibit obvious differences in electrochemical behaviors. That may point the feasible way to purposive synthesis of solid material with special properties by varying some ingredient.

### 3.4. Thermogravimetric (TG) analyses.

In order to estimate the thermal stability of title compounds, the TG analyses experiments were performed under  $\text{N}_2$  atmosphere with a heating rate of  $10^\circ\text{C}/\text{min}$  in the temperature range of 25–800  $^\circ\text{C}$ , as shown in Fig. S10. There is only one obvious



**Fig. 8.** (a) Cyclic voltammograms for (a) the bare CPE in 1 M  $\text{H}_2\text{SO}_4+8.0 \text{ mM NO}_2^-$  solution and the **1**-CPE in 1 M  $\text{H}_2\text{SO}_4$  aqueous solution containing (b) 0, (c) 1.0, (d) 2.0 and (e) 4.0 mM  $\text{NO}_2^-$ . Scan rate:  $300 \text{ mV s}^{-1}$ ; (b) Cyclic voltammograms for (a) the bare CPE in 1 M  $\text{H}_2\text{SO}_4+8.0 \text{ mM NO}_2^-$  solution and the **2**-CPE in 1 M  $\text{H}_2\text{SO}_4$  aqueous solution containing (b) 0, (c) 1.0, (d) 2.0 and (e) 4.0 mM  $\text{NO}_2^-$ . Scan rate:  $300 \text{ mV s}^{-1}$ ; (c) Cyclic voltammograms for (a) the bare CPE in 1 M  $\text{H}_2\text{SO}_4+8.0 \text{ mM NO}_2^-$  solution and the **3**-CPE in 1 M  $\text{H}_2\text{SO}_4$  aqueous solution containing (b) 0, (c) 1.0, (d) 2.0, and (e) 4.0 mM  $\text{NO}_2^-$ . Scan rate:  $300 \text{ mV s}^{-1}$ .

weight loss step in each compound, which is ascribed to the loss of organic ligands. The weight loss step occurred between 200 and 280 °C by 24.9% (calcd 23.3%) for **1**, 180–320 °C by 22.1% (calcd 21.0%) for **2**, 200–340 °C by 30.4% (calcd 28.8%) for **3**.

#### 4. Conclusion

In this paper, three Keggin-type POM-based Cu<sup>I</sup>–bmtr complexes have been synthesized under hydrothermal conditions. Crystal structure analyses reveal that two kinds of different structures have been obtained by tuning the types of Keggin polyanions. When the SiMo<sub>12</sub> is utilized, we can obtain a (3, 4)-connected 3D framework of compound **1**, which contains tetranuclear subunits. Otherwise, if the PW<sub>12</sub> and PMo<sub>12</sub> polyanions are selected instead of SiMo<sub>12</sub>, isostructural 1D chain-like compounds **2** and **3** were constructed, which contain trinuclear subunits. This work shows that tuning the types of Keggin polyanions is an effective strategy in crystal engineering of preparing POM-based inorganic–organic hybrid compounds. Further study on other type polyanions is underway, such as Wells–Dawson and Anderson polyanions.

#### Supporting information

Tables of selected bond lengths and angles for compounds **1–3**; TGA curves, dependence lines of cathodic peak and anodic peak currents on scan rates for **1**-, **2**- and **3**-CPEs, dependence curves of reduction peak currents III on concentration of nitrite and structural figures of compounds **1–3**.

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#### Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2012.01.0014.

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