

Cite this: *CrystEngComm*, 2012, **14**, 3125

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PAPER

External template-assisted self-assembly: design and synthesis of the $[\text{MoOS}_3\text{Cu}_3]^+$ based supramolecular polymeric clusters†

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Received 12th November 2011, Accepted 20th January 2012

DOI: 10.1039/c2ce06518e

Four novel heterothiometallic cluster polymers based on a $[\text{MoOS}_3\text{Cu}_3]$ unit have been synthesized by the solution self-assembly of 4,4'-bipy (4,4'-bipy = bpy) with $[\text{NH}_4]_2\text{MoS}_2\text{O}_2$ and CuX ($\text{X} = \text{I}, \text{Br}$, or SCN) in the presence of different organic cation-templates $[\text{DMI}] \cdot \text{I}$, $[\text{C}_6(\text{Mim})_2] \cdot \text{Br}_2$, $[\text{C}_3(\text{Mim})_2] \cdot \text{Br}_2$, and $[\text{BBP}] \cdot \text{Br}_2$: Compounds $\{[\text{MoOS}_3\text{Cu}_3\text{I}(\mu\text{-bpy})_{2.5}] \cdot 2.5\text{DMF}\}_\infty$ (**1**), $\{[\text{MoOS}_3\text{Cu}_3\text{I}(\mu\text{-bpy})_{2.5}] \cdot \text{DMF}\}_\infty$ (**2**), and $\{[\text{MoOS}_3\text{Cu}_3\text{Br}(\mu\text{-bpy})_{2.5}] \cdot 2.5\text{DMF}\}_\infty$ (**3**) are isomorphous neutral 3D 4-fold interpenetrating architectures with a (6, 4) node, while polymer $[\text{MoOS}_3\text{Cu}_3(\text{NCS})(\mu\text{-bpy})_{2.5}]_\infty$ (**4**) is a 3D architecture with a $(6^4 8^2)$ net displaying self-interpenetrating features. All of them have been characterized by single-crystal X-ray diffraction, elemental analysis, IR, TGA, and UV-vis. The results may provide fascinating insights into the template effect on the construction of the cluster-based coordination polymers.

Introduction

The term template effect was first used and defined at the beginning of the sixties.¹ More and more examples found in the literature cover the relevance of the template effect under the heading of rational synthesis.^{2,3} In addition to metal ions that can act as templates, neutral molecules, hydrogen bonds, electrostatic interactions also support the formation of binary and tertiary complexes.^{4,5} Apart from the definition around a metal ion, specific atoms or molecular groups can also be construed as templates.⁶ A template is described as temporary or external if it is eliminated at the end of a synthesis and is therefore not incorporated into the end product.⁷ If the molecular compounds originally present are also found in the end product, it can be defined as a permanent template. On the other hand, in the past decades, one interesting category is those of Mo(W)/Cu/S cluster-based units that are assembled with inorganic bridging (S^{2-} , Cl^- , Br^- , I^- , SCN^- , CN^-) or pyridinyl-, pyrazolyl- and imidazolyl-based linkers.^{8–14} Most of these heterothiometallic polymeric compounds are filled with organic or inorganic cations with low charge density and small size (of course with less template effect), such as NH_4^+ and $[\text{RNH}_3]^+$ (R = organic groups). But what would be produced if larger size and higher symmetry charged organic cations were used?

A bolaamphiphile is simply defined as a molecule in which two or more hydrophilic groups are connected by hydrophobic functionalities.¹⁵ Symmetric R,ω -bolaamphiphiles possess far-ranging applications as constituents of multilayer structures, vesicle membranes and amphiphilic crystals.¹⁶ Up to now, we have used the 1, ω -bis(pyridinium)alkane cation-templated synthesis in the construction of polymer thiocyanates,^{17a,b} polyoxometalate frameworks,^{17c} and Mo(W)/Cu/S -based clusters.^{17d–f} In this paper, we report a variation of above studies and selected 1, 3-bis(imidazole)propane, and 1, 6-bis(imidazole)hexane as new cation-templates and two novel heterothiometallic $[\text{MoOS}_3\text{Cu}_3]$ -based polymers **2** and **3** with a 4-fold interpenetrating neutral diamondoid network^{9a,10a} were obtained, respectively. As a comparison, we also selected non-bolaamphiphile molecules as cation-templates and obtained two new compounds **1** and **4**. Polymer **1** is also a 4-fold interpenetrating neutral diamondoid framework, whereas compound **4** is a self-interpenetrating 3D network.

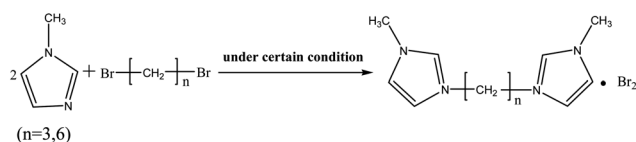
Experimental

General procedures

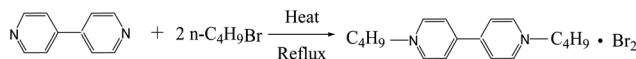
The starting material $[\text{NH}_4]_2\text{MoS}_2\text{O}_2$ was prepared as described in the literature.¹⁸ The organic dications $[\text{C}_3(\text{Mim})_2] \cdot \text{Br}_2$ (1,1'-dimethyl-3, 3'-(1, 3-trimethylene) bisimidazolium-dichloride) and $[\text{C}_6(\text{Mim})_2] \cdot \text{Br}_2$ (1,1'-(hexane-1, 6-diyl) bis(3-methyl-1H-imidazolium-1-yl) dibromide) were synthesized as reported previously^{19,20} except using dibromine alkyl instead of the dichlorine alkane and the reaction route is shown in Scheme 1. The cation BBP^{2+} was synthesized as described in the literature,²¹ which reaction route is shown in Scheme 2. The organic cation

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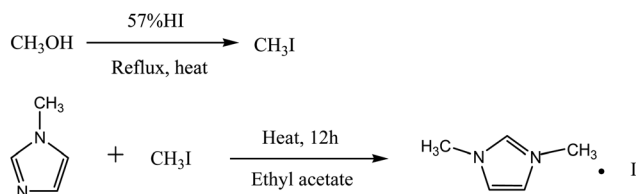
† Electronic supplementary information (ESI) available: TGA curves, experimental and detailed crystallographic data and structural refinement parameters for **1–4**. CCDC reference numbers 845162–845165. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce06518e



Scheme 1



Scheme 2



Scheme 3

[DMI]⁺ was synthesized as reported in the literature²² and the reaction route is shown in Scheme 3. All chemicals and solvents are of A.R. grade and used without further purification. The IR spectrum was recorded on a Shimadzu IR435 spectrometer as a KBr disk (4000–400 cm^{−1}). Elemental analysis was carried out on a Vario EL III elemental analyzer (C, H, N, S). Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300 DV ICP instrument (Mo, Cu). A model NETZSCH TG209 thermal analyzer was used to record simultaneous TG, DSC curves in the flowing air atmosphere of 20 mL min^{−1} at a heating rate of 5 °C min^{−1} in the temperature range r. t.–800 °C using platinum crucibles. UV-vis measurement of **1–4** in DMF solution was conducted on a HP-8453 spectrophotometer and the data is collected at room temperature.

Experimental section

Preparation of {[MoOS₃Cu₃I(μ-bpy)_{2.5}]·2.5DMF}_∞ (1**).** A mixture of [NH₄]₂MoS₂O₂ (0.114g, 0.5 mmol), 4,4'-bipy (0.078g, 0.5 mmol), DMI·I (0.168g, 0.75mmol) and CuI (0.191g, 1.0mmol) in DMF was stirred at 90 °C for 10 h. Then the reaction solution was filtered and left to stand in darkness. Dark-red blocky-shaped crystals were obtained at ambient temperature one week later. Yield: 0.0684g (60% based on Mo). Anal. calcd. (%) for C₃₁H₃₄O₃S₃MoICu₃N₇: C, 35.03; H, 3.20; N, 9.23; Mo, 9.02; S, 9.04; Cu, 17.93. Found: C, 35.00; H, 3.24; N, 9.25; Mo, 9.10; S, 9.12; Cu, 17.88. IR (KBr, cm^{−1}): 3421 (w), 1655 (m), 1600 (s), 1408 (s), 1215 (m), 1064 (m), 908 (m), 807 (s), 628 (m), 438 (m).

Preparation of {[MoOS₃Cu₃I(μ-bpy)_{2.5}]·DMF}_∞ (2**).** Red crystals were obtained under conditions similar to those for **1** only with [C₆(Mim)₂]·Br₂ (0.408g, 1.0mmol) instead of [DMI]·I. Yield: 37% (based on Mo). Anal. calcd. (%) for C₂₈H₂₇Cu₃IMoN₆O₂S₃: C, 33.95; H, 2.78; N, 8.64; Mo, 9.66; S, 9.73; Cu, 19.26. Found: C, 33.86; H, 2.77; N, 8.66; Mo, 9.72; S, 9.68; Cu, 19.33. IR (KBr, cm^{−1}): 3431 (m), 3033 (w), 1663 (s), 1598 (s),

1483 (m), 1408 (s), 1253 (w), 1063 (m), 905 (m), 802 (s), 626 (m), 569 (w), 435 (s).

Preparation of {[MoOS₃Cu₃Br(μ-bpy)_{2.5}]·2.5DMF}_∞ (3**).** Dark red crystals were obtained under conditions similar to those for **2** only with [C₃(Mim)₂]·Br₂ and CuBr instead of [DMI]·I and CuI, respectively. Yield: 40% (based on Mo). Anal. calcd. (%) for C_{32.5}H₃₄BrCu₃MoN_{7.5}O_{3.5}S₃: C, 37.21; H, 3.24; N, 10.02; Mo, 9.14; S, 9.15; Cu, 18.19. Found: C, 37.21; H, 3.23; N, 10.04; Mo, 9.18; S, 9.16; Cu, 18.12. IR (KBr, cm^{−1}): 3432 (m), 3032 (w), 1663 (s), 1598 (s), 1529 (w), 1408 (s), 1253 (w), 1215 (m), 1063 (m), 905 (m), 807 (s), 626 (m), 436 (s).

Preparation of [MoOS₃Cu₃(NCS)(μ-bpy)_{2.5}]_∞ (4**).** Under condition similar to those for **2**, compound **4** was obtained except using BBP·Br₂ and CuSCN instead of [DMI]·I and CuI, respectively. Yield: 57% (based on Mo). Anal. calcd. (%) for C₂₆H₂₀Cu₃MoN₆O₄S₃: C, 36.82; H, 2.36; N, 9.91; Mo, 11.33; S, 15.13; Cu, 22.51. Found: C, 36.90; H, 2.34; N, 9.98; Mo, 11.42; S, 15.22; Cu, 22.62. IR (KBr, cm^{−1}): 3424 (w), 1664 (m), 1600 (s), 1410 (s), 1217 (m), 1066 (m), 903 (m), 806 (s), 628 (m), 439 (s).

X-ray crystallography study

Crystallographic data and structural refinements for **1–4** are summarized in detail in Table 1. The intensity data for four compounds were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 296(2) or 291.1 K. Absorption corrections were applied by using SADABS. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restraints. The structures were solved by direct methods with the SHELXS-97 program.²³ Important bond lengths and angles are given in Table S1.†

Results and discussion

Synthesis

The template method is widely used in the synthesis of coordination polymers and has received more widespread attention.²⁴ Because of the use of templates, on the one hand reactions that could not previously be conducted were able to be carried out, and on the other, the polymer structures obtained became more diversified and intriguing. Recently, our group focused on constructing elaborate structures directed by an organic cation-template in the presence of [NH₄]₂MoS₂O₂, copper(i) sources and 4,4'-bipy linkers. A series of interesting results were obtained, such as, {(bppp)[MoOS₃Cu₃I₃(4,4'-bipy)_{1.5}]}_∞, {(bpbtp)[MoOS₃Cu₃I₃(4,4'-bipy)_{1.5}]}_∞, {(bppp)[WOS₃Cu₃I₃(4,4'-bipy)_{1.5}]}_∞, and {(bpbtp)[WOS₃Cu₃Br₃(4,4'-bipy)_{1.5}]}_∞^{17e} with one-dimensional zigzag chains; {[Mo₂O₂S₆Cu₆BrI(4,4'-bipy)₄](4,4'-bipy)}_∞ and {[WOS₃Cu₃Br(4,4'-bipy)_{2.5}]·3(DMF)}_∞ with neutral 3D 3–4 fold interpenetrating architectures;^{17f} [MoO-S₃Cu₃Cl(μ-bpy)₂·1.3DMF·5.5H₂O]_∞, [WOS₃Cu₃Cl(μ-bpy)₂·1.5DMF·8.2H₂O]_∞, [MoOS₃Cu₃(NCS)(bpy)(μ-bpy)₂·DMF]_∞, and [WOS₃Cu₃(NCS)(μ-bpy)_{2.5}·3DMF]_∞ with 2–3D non-interpenetrating or self-interpenetrating networks.^{17d} In the synthesis of these compounds, the bipyridinium templates played an

Table 1 Crystal data and structure refinement for **1–4**

Compounds	1	2	3	4
Formula	C ₃₁ H ₃₄ O ₃ S ₃ MoICu ₃ N ₇	C ₂₈ H ₂₇ Cu ₃ IMoN ₆ O ₂ S ₃	C _{32.5} H ₃₄ N _{7.5} MoO _{3.5} Cu ₃ BrS ₃	C ₂₆ H ₂₀ Cu ₃ MoN ₆ OS ₄
Formula weight	1062.30	989.22	1048.32	847.30
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> /Å	21.2500(10)	21.186(5)	21.263(2)	40.592(8)
<i>b</i> /Å	21.2819(8)	21.293(5)	21.2870(18)	9.7008(19)
<i>c</i> /Å	18.1026(7)	17.947(4)	18.0287(17)	24.750(5)
α (°)	90	90	90	90
β (°)	96.336(4)	96.459(18)	96.213(10)	104.95(3)
γ (°)	90	90	90	90
Volume/Å ³	8136.7(6)	8045(3)	8112.2(13)	9416(3)
<i>Z</i>	4	4	4	4
Calculated density/Mg m ^{−3}	1.734	1.513	1.717	1.195
μ /mm ^{−1}	2.800	2.814	3.037	1.795
<i>F</i> (000)	4184	3544	4172	3352
Crystal size/mm	0.30 × 0.30 × 0.25	0.43 × 0.32 × 0.27	0.23 × 0.22 × 0.21	0.23 × 0.21 × 0.18
<i>T</i> /K	291.0	296(2)	291.15	296(2)
Reflections collected	18816	46399	28647	45938
Independent reflections	8301	7363	8279	8255
Data/restraints/parameters	8301 / 4 / 410	7363 / 0 / 352	8279 / 12 / 447	8255 / 0 / 370
Goodness-of-fit on <i>F</i> ²	1.048	1.096	1.022	1.000
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0511 <i>wR</i> ₂ = 0.1197	<i>R</i> ₁ = 0.0818 <i>wR</i> ₂ = 0.2246	<i>R</i> ₁ = 0.0502 <i>wR</i> ₂ = 0.1202	<i>R</i> ₁ = 0.0606 <i>wR</i> ₂ = 0.1363
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0750 <i>wR</i> ₂ = 0.1324	<i>R</i> ₁ = 0.1096 <i>wR</i> ₂ = 0.2739	<i>R</i> ₁ = 0.0896 <i>wR</i> ₂ = 0.1408	<i>R</i> ₁ = 0.0946 <i>wR</i> ₂ = 0.1505
Largest peak	1.128	2.226	1.14	0.444
Hole/e Å ^{−3}	−0.778	−2.645	−0.51	−0.374

important role. In this contribution we chose the imidazole template and got three new polymeric clusters **1**, **2**, and **3**. They are isomorphous 3D complexes with a 4-fold interpenetrating framework; Interestingly, when we used another type of bipyridinium derivative template a self-interpenetrating 3D compound **4** was obtained. So based on this study it seems that the imidazole template has more advantages than the pyridinium template. For instance, the structure of these compounds are more elaborate in the presence of an imidazole cation regardless of the template size, large or small; However, only a dipyrindinium template possessing a large volume can bring these entanglements.

Description of crystal structures

Crystal structures of polymers 1, 2, 3. Polymers **1**, **2**, and **3** are isostructural, and have a similar chemical formula, namely, {[MoOCu₃S₃I(μ-bpy)_{2.5}]·2.5DMF}_{*n*}, {[MoOS₃Cu₃I(μ-bpy)_{2.5}]·DMF}_{*n*}, and, {[MoOS₃Cu₃Br(μ-bpy)_{2.5}]·2.5DMF}_{*n*}, respectively. In **1** one of the bpy ligands lies about a twofold axis and the asymmetric unit has two DMF molecules in general positions and one half bpy lying disordered about a twofold axis. In **3** one of the bpy ligands lies about a twofold axis and the asymmetric unit has two DMF molecules in general positions and one lying disordered about a twofold axis. Their cell parameters are essentially identical, therefore, only the structure of polymer **2** is described in detail. The X-ray single crystal structural analysis²³ showed that polymer **2** crystallizes in the monoclinic system with the space group *C2/c*. The asymmetric unit includes the

incomplete cubane-like secondary building units (SBUs) [MoO-S₃Cu₃], two and a half molecules of bridging ligands bpy, and one terminal I atom and one of the bpy ligands lies about a twofold axis (as shown in Fig. 1a). From Fig. 1b, it can be easily learnt that the 6-membered circuit is constructed by repeating the [MoOS₃Cu₃] core and four single-bridging ligands bpy and two double-bridging ligands bpy. This packing arrangement results in large channels created along the *ac* plane with dimensions of 21.186 Å × 20.581 Å, which provides an advantageous condition for the formation of a 4-fold interpenetrating network.

In polymer **2**, all the Cu atoms adopt a distorted tetrahedral coordination geometry and each SBUs serves as a tetrahedral four-connecting node and is coordinated by five bidentate ligands bpy, which link four crystallographically equivalent SBUs (Fig. 1c), and furthermore forming a single diamondoid type unit (Fig. 1d). This unit is further interconnected by bpy bridges to form a unique 3D diamondoid network. From the topological perspective (Fig. 1e), we found polymer **2** is a 4-fold interpenetrating neutral diamond network, which can be reduced to a 4-connected (6, 4) net. To our knowledge, there are two examples with the 4-fold interpenetrated 3D net, {[WS₄Cu₄(4,4'-bipy)₄][WS₄Cu₄I₄(4,4'-bipy)₂]}_{*n*} and {[WS₄Cu₄(4,4'-bipy)₄][WS₄Cu₄I₄(4,4'-bipy)₂]·4H₂O}_{*n*}.^{9a,10a} But the latter two compounds contain interpenetrating cationic and anionic 3D diamondoid cluster coordination polymers. So compounds **1–3** may provide representative examples for the facile construction of this type of high dimensional architectures with simple external templates.

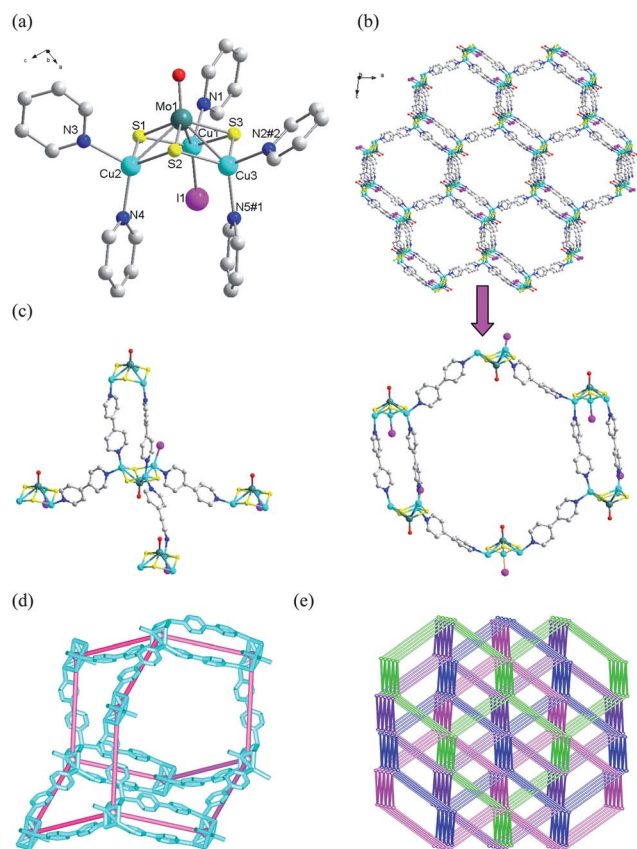


Fig. 1 (a) The symmetric unit of **2**. Symmetry codes: #1: $-x + 1, y, -z + 3/2$. #2: $-x + 1/2, y + 1/2, -z + 1/2$. (b) A perspective view of the 3D network in **2** along the *ac* plane, which contains the 6-membered ring. All hydrogen atoms are omitted for clarity. Symmetry codes: #1: $-x + 1, y, -z + 3/2$. #2: $-x + 1/2, y + 1/2, -z + 1/2$. #3: $-x + 1/2, y - 1/2, -z + 1/2$. #4: $-x, y, -z + 3/2$. (c) View of the interactions of a $[\text{MoOS}_3\text{Cu}_3\text{I}]$ core via a double μ -bpy bridge and three single-bridging ligands μ -bpy in **2**. (d) View of a highly distorted diamondoid unit within the network of **2**. (e) Overall a 4-fold interpenetrating 4-connected (6, 4) topology of compounds **2**. Each node and rod represents a cluster fragment $[\text{MoO-S}_3\text{Cu}_3]$ and μ -bpy ligands, respectively.

Crystal structure of polymer 4. When DMI-I and CuI were replaced by $[\text{BBP}]\cdot\text{Br}_2$ and CuSCN, a structurally different polymer **4** was obtained. Single-crystal X-ray diffraction analysis revealed that polymer **4** shows a novel 3D self-interpenetrating structure. It crystallizes in the monoclinic system with the space group $C2/c$. As shown in Fig. 2a, the asymmetric unit contains only $[\text{MoOS}_3\text{Cu}_3(\text{NCS})(\mu\text{-bpy})_{2.5}]$ molecule, and one of the bpy ligands lies about a twofold axis. The nest-shaped $[\text{MoOS}_3\text{Cu}_3]$ cluster core is connected by two and a half bridging bpy molecules and one terminal NCS anion via three Cu atoms, which links four crystallographically equivalent clusters via four bridging bpy molecules to form a 3D network structure. In the net two types of 6-membered and 8-membered circuits are included and the six-membered ring intersperses with the other six-membered ring and eight-membered ring (Fig. 2b).

Topologically, the 3D self-interpenetrating network of **4** can be abbreviated to a 4-connected ($6^4 8^2$) net (Fig. 2c), which is different from the non-exclusive list of 4-connected twisted

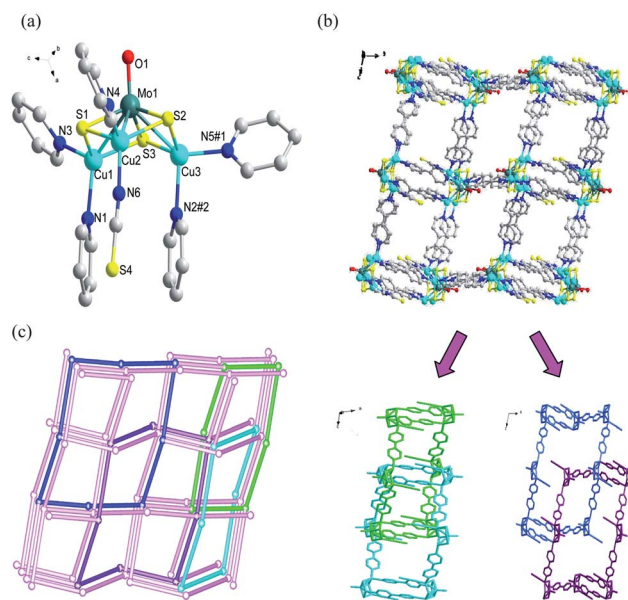


Fig. 2 (a) The asymmetric unit of **4**. Symmetry codes: #1: $x, -y + 2, z - 1/2$. #2: $-x + 1/2, -y + 1/2, -z$. (b) A perspective view of the 3D network in **4** along the *ac* plane, which contains 6-membered and 8-membered rings. All hydrogen atoms are omitted for clarity. Symmetry codes: #1: $x, -y + 2, z - 1/2$. #2: $-x + 1/2, -y + 1/2, -z$. #3: $x, -y + 2, z + 1/2$. #4: $-x, -y, -z$. (c) The overall self-interpenetrating 4-connected ($6^4 8^2$) topology of polymer **4**. Each node and rod represents a cluster fragment $[\text{MoO-S}_3\text{Cu}_3(\text{NCS})]$ and 4,4'-bipy ligand, respectively.

dia, nbo, pts, and qtz nets²⁵ because polymer **4** exhibits a self-interpenetrating network topology, as mentioned above, the six-membered ring intersperses with the other six-membered ring and the eight-membered ring, which is also interesting. To the best of our knowledge, for self-interpenetrating 3D compounds, only two examples have been reported: one is compound **4**, the other is $[\text{WOS}_3\text{Cu}_3(\text{NCS})(\mu\text{-bpy})_{2.5}\cdot 3\text{DMF}]_n$.^{17d} However, in the latter one the central metal atom is the tungsten, which probably causes the presence of DMF solvent molecules. It is worth mentioning that **4** is quite similar to the 3D example $\{[\text{MoO-S}_3\text{Cu}_3(\text{NCS})(4, 4'\text{-bipy})_{2.5}\cdot 3(\text{ani})]\}_n$ by chemical formula.²⁶ However, the later polymer holds a 3-fold interpenetrated 3D diamondoid net in which each cluster core also works as a tetrahedral 4-connecting node and is coordinated by five bridging ligands 4,4'-bipy. And, furthermore, the voids of the cell are occupied by the aniline solvent molecules.

TGA

In order to characterize this type of polymer more fully in terms of the thermal decomposition behavior, TGA experiments of **1** and **2** were carried out up to 850 °C in a flowing air atmosphere, and their TGA curves are shown in Fig. S1–2.† From the curves of **1**, the weight loss of 29% in the range 115–240 °C could be assigned to the escape of the DMF molecules and a portion of the decomposition of organic components. Above this temperature, the second stage commences from the range 290–450 °C, corresponding to losses of the remaining organic portion. Analysis of the curve of **2** reveals that the initial weight loss of ca. 7.20% at 235 °C is close to the theoretical value 7.38% (losing one DMF

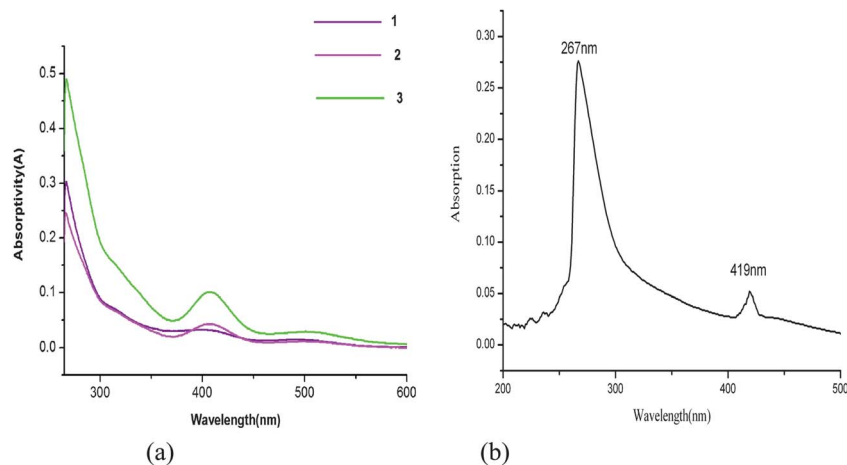


Fig. 3 (a): UV-vis curves for the DMF solutions of 10^{-5} M for **1–3**. (b): UV-vis curves for the DMF solutions of 10^{-5} M for **4**.

molecule), above this temperature, the second step of weight loss is due to the decomposition of organic components.

UV-vis absorption spectra of **1–4**

The study of UV-vis properties of **1–4** in DMF solution was carried out on a HP-8453 spectrophotometer at room temperature and the spectra charts are shown in Fig. 3. The electronic spectra of **2**, **3**, and **4** show a weak peak at 406 nm, 408 nm, and 419 nm, respectively, which may be attributed to the $S \rightarrow Mo$ charge transition in the $[MoOS_3]$.^{27a} What's more, in the UV-vis absorbance spectrum of these four compounds, there are strong characteristic absorption peaks at 266.50 nm (**2**), 267 nm (**1**, **3**, and **4**). According to the literature we have consulted, the strong absorption peaks may be caused by the metal-to-ligand charge transfer transition.^{27b}

Conclusions

In this paper, we reported four cluster polymers and demonstrated our efforts to explore the synthetic approaches on the assembly of $[MoOS_3Cu_3]$ -based coordination polymers. Although we selected different templates, polymers **1**, **2**, and **3** are neutral three-dimensional four-fold interpenetrating diamondoid network structures and polymer **4** is a 3D self-interpenetrating network. In addition, the template does not exist in polymers **1**, **2**, **3**, and **4**, which may be due to the three-dimensional interpenetrating spatial network structure. Our studies have demonstrated that the cationic template effect plays a very crucial role in building these heterothiometallic polymeric clusters. When they act as a temporary template, the neutral 4-fold interpenetrating diamondoid network and self-interpenetrating network don't have enough cavities to accommodate them, so the cation-template has to leave the product after it finishes the induction or directing template effects.

Further efforts are in progress to extend these organic cations to other polymeric clusters, and investigate into the assembly of new $[Mo/WS_4Cu_4]$ or $[Mo/WS_3Cu_3]$ -based heterothiometallic polymer by using different 1, ω -bis(imidazole)alkane cations and macrocyclic organic cations.

Acknowledgements

Research efforts in the Niu group are supported by the National Science Foundation of China (No. 20671083, 21171148).

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