Inorg. Chem. **2008**, *47*, 529–534

Inorganic Chemistry
Article

Supramolecular Isomerism with Polythreaded Topology Based on $[Mo_8O_{26}]^{4-}$ Isomers

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Received July 23, 2007

Two compounds, namely, $[Cu(bbi)]_2[Cu_2(bbi)_2(\delta\text{-}Mo_8O_{26})_{0.5}][\alpha\text{-}Mo_8O_{26}]_{0.5}$ (**1**) and $[Cu(bbi)][Cu(bbi)(\theta\text{-}Mo_8O_{26})_{0.5}]$ (**2**), where bbi is 1,1′-(1,4-butanediyl)bis(imidazole), were synthesized under hydrothermal conditions at different pH values. Their crystal structures were determined by X-ray diffraction. Compounds **1** and **2** are supramolecular isomers with a polythreaded topology based on octamolybdate building blocks.

Introduction

Supramolecular isomerism can be a consequence of the effect of the same molecular components generating different supramolecular synthons and could be synonymous with polymorphism. It is one of the most important aspects of supramolecular chemistry, which has attracted great interest because of not only its structural diversity but also its potential application in recent years.[1] Zaworotko and Moulton have examined the occurrence of supramolecular isomerism.[2] The design of a molecular building block for supramolecular isomers with a fixed chemical stoichiometry is difficult since many factors can influence the composition.[3] Therefore, the synthesis of supramolecular isomers should be regarded as a significant research topic in understanding supramolecular isomerism and crystal growth.[4] Of concurrent interest has been the construction of the entangled system as defined by Ciani and co-workers.[5a,c] The entangled system includes interpenetration, polycatenation, polythreading, polyknotting, and so on.[5a] Polythreaded structures are characterized by the presence of closed loops, as well as of elements that can thread through the loops, and can be considered as extended periodic analogues of molecular rotaxanes and pseudorotaxanes.[5f] A few coordination compounds exhibiting polythreaded network architectures have been reported.[5a,f,6] However, supramolecular isomerism with a polythreaded topology has not been observed, although an enormous number of isomers is known in classical coordination chemistry.[1−4]

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10.1021/ic701463h CCC: $40.75

On the other hand, polyoxometalates (POMs) have been extensively studied due to their intriguing properties in chemistry, physics, biology, and material science.[7] Of the various POM structures, polyoxomolybdate is a remarkable member of this family due to its diverse structures.[8] Octamolybdates are one important branch in the polyoxomolybdate chemistry due to their varied structural patterns in the solid state. To date, eight isomeric forms of octamolybdates have been prepared, that is, the α-, β-, γ-, δ-, ϵ-, ζ-, η-, and θ-isomers.[9] It is an interesting and unusual phenomenon that there are two forms of octamolybdate isomers in one compound. Our group has reported this kind of compound that contains the α- and β-isomers.[10] As reported previously, the pH value of the reaction system is crucial for the formation of the previously mentioned isomers.[9b,11] Recently, octamolybdates have widely been regarded as an important molecular building unit for inorganic−organic coordination polymers. A variety of POM-based coordination polymers has successfully been assembled through octamolybdate covalently linked with metal-organic units.[9] However, there has been a lack of investigation on supramolecular isomerism using POM-based coordination polymers. Up to now, octamolybdate-based supramolecular isomers have not been observed.

As accurate prediction of the final superstructures is impossible, we attempted different synthetic conditions to study the possible supramolecular isomerism. In our strategy, octamolybdate and flexible ligands with different characters were chosen based on the following considerations: (i) Octamolybdate with a variety of structural isomers at different pH values may induce the formation of various structural types and (ii) conformational changes in flexible ligands generate a different but often related network architecture, and it often leads to supramolecular isomers[2,3a] and can more easily produce these new classes of compounds. In view of these points, we have performed many experiments. Fortunately, compounds $[Cu(bbi)]_2[Cu_2(bbi)_2(\delta\text{-}Mo_8O_{26})_{0.5}][\alpha\text{-}Mo_8O_{26}]_{0.5}$ (**1**) and $[Cu(bbi)(\theta\text{-}Mo_8O_{26})_{0.5}][Cu(bbi)]$ (**2**) were isolated successfully by hydrothermal methods at different pH values. These two products are very stable in air and begin to decompose when heated to as high as 377 °C for **1** and 370 °C for **2**, respectively (Figure S1). To the best of our knowledge, they represent a new type of supramolecular isomerism with a polythreaded topology based on octamolybdate building blocks.

Experimental Procedures

Materials. All reagents and solvents used for the syntheses were purchased from commercial sources and used as received.

General Characterization and Physical Measurements. The C, H, and N elemental analyses were conducted on a Perkin−Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 4000−400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. TGA was performed on a Perkin−Elmer TG-7 analyzer heated from room temperature to 1200 °C under nitrogen. Solid-state fluorescence spectra were recorded on a Cary Eclipse spectrofluorometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature.

Syntheses of $[Cu(bbi)]_2[Cu_2(bbi)_2(\delta\text{-}Mo_8O_{26})_{0.5}][\alpha\text{-}Mo_8O_{26}]_{0.5}$ (1). A mixture of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.124 g, 0.1 mmol), bbi (0.095 g, 0.5 mmol), $Cu(NO_3)_2\cdot 3H_2O$ (0.121 g, 0.5 mmol), and H_2O (10 mL) was adjusted to approximately pH ≈ 4−5 with dilute Et_3N solution and hydrochloric acid and stirred for 1 h and then was transferred and sealed in a 25 mL Teflon-lined stainless steel container. This container was heated at 150 °C for 72 h and then cooled to room temperature at a rate of 10 °C h^{-1}. Yellow crystals of **1** were collected in 42.6% yield based on $Cu(NO_3)_2\cdot 3H_2O$. Elemental analyses calcd for $C_{40}H_{56}Cu_4Mo_8N_{16}O_{26}$ (2198.69): C, 21.85; H, 2.57; N, 10.19. Found: C, 21.82; H, 2.56; N, 10.20. IR (cm^{-1}): 3416 (m), 3113 (m), 2359 (w), 1520 (w), 951 (m), 908 (s), 797 (s), 647 (s).

Syntheses of $[Cu(bbi)(\theta\text{-}Mo_8O_{26})_{0.5}][Cu(bbi)]$ (2). The same synthetic procedure as that for **1** was used except for pH ≈ 2. Yellow crystals of **2** were collected in 42.6% yield based on $Cu(NO_3)_2\cdot 3H_2O$. Elemental analyses calcd for $C_{20}H_{28}Cu_2Mo_4N_8O_{13}$ (1099.34): C, 21.85; H, 2.57; N, 10.19. Found: C, 21.83; H, 2.59; N, 10.18. IR (cm^{-1}): 3416 (m), 3113 (m), 2360 (w), 1524 (w), 951 (m), 908 (s), 796 (s), 647 (s).

X-ray Crystallography. Single-crystal X-ray diffraction data for **1** and **2** were recorded on a Bruker Apex CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Absorption corrections were applied using a multiscan technique. All the structures were solved by Direct Methods in SHELXS-97[12] and refined by a full-matrix least-squares techniques using the SHELXL-97 program[13] within WINGX.[14] Non-hydrogen atoms

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Table 1. Crystal Data and Details of Data Collection and Refinement for Isomers **1** and **2**

	1	**2**
Formula	$C_{40}H_{56}Cu_4Mo_8N_{16}O_{26}$	$C_{20}H_{28}Cu_2Mo_4N_8O_{13}$
Fw	2198.69	1099.34
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.5120(5)	11.9100(19)
b (Å)	13.2800(5)	12.458(2)
c (Å)	19.8050(7)	13.113(2)
α (deg)	95.6900(10)	70.031(3)
β (deg)	101.2070(10)	63.821(2)
γ (deg)	91.5290(10)	69.960(3)
V (Å^3)	3208.6(2)	1598.0(4)
Z	2	2
D_{calcd} (g cm^{-}3)	2.276	2.285
$F(000)$	2136	1068
reflns collected/unique	16131/11203	7852/5574
GOF on F^2	1.007	1.062
R(int)	0.0223	0.0240
$R_1{}^a$ $[I > 2\sigma(I)]$	0.0388	0.0754
$wR_2{}^b$	0.0774	0.1764

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

were refined with anisotropic temperature parameters. The hydrogen atoms of the organic ligands were refined as rigid groups. The detailed crystallographic data and structure refinement parameters for **1** and **2** are summarized in Table 1.

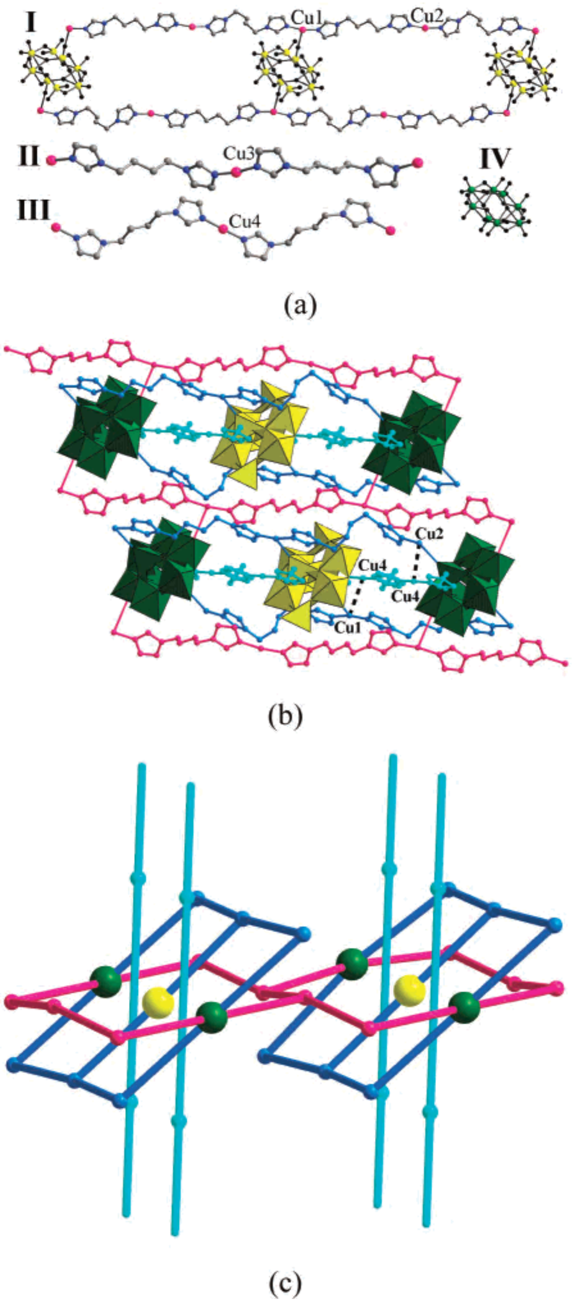

Figure 1. (a) Ball-and-stick representation of four kinds of subunits: $[Cu_2(bbi)_2(\delta\text{-}Mo_8O_{26})_{0.5}]_\infty$, two kinds of $[Cu(bbi)]^+{}_\infty$ coordination polymeric compositions, and isolated $[\alpha\text{-}Mo_8O_{26}]^{4-}$ counterions. (b) Ball-and-stick and polyhedral representations of the polythreaded structure in **1**. (Yellow and green polyhedra represent $[\delta\text{-}Mo_8O_{26}]^{4-}$ and $[\alpha\text{-}Mo_8O_{26}]^{4-}$ polyoxoanions, respectively, and black dashed lines represent Cu^I-Cu^I interactions between two $[Cu(bbi)]^+{}_\infty$ chains.) (c) Schematic representation of the polythreaded structure in **1**. (Yellow and green balls represent $[\delta\text{-}Mo_8O_{26}]^{4-}$ and $[\alpha\text{-}Mo_8O_{26}]^{4-}$ polyoxoanions, respectively, and cyan pillars represent $[Cu_4(bbi)]^+{}_\infty$ chains.)

Results and Discussion

Structure Description of 1. Single-crystal X-ray diffraction analysis reveals that four kinds of subunits cocrystalize in **1** (Figure 1a). As such, there exist four kinds of Cu^I cations and bbi ligands, and two kinds of $[Mo_8O_{26}]^{4-}$ polyoxoanions ($[\alpha\text{-}Mo_8O_{26}]^{4-}$ and $[\delta\text{-}Mo_8O_{26}]^{4-}$).[9b,c] The typical $[\alpha\text{-}Mo_8O_{26}]^{4-}$ polyoxoanion consists of a ring of six edge-sharing $\{MoO_6\}$ octahedra capped at the poles by two $\{MoO_4\}$ tetrahedra.[10] Three kinds of oxygen atoms exist in the $[\alpha\text{-}Mo_8O_{26}]^{4-}$ polyoxoanion, that is, the terminal oxygen atoms, double-bridging oxygen atoms, three-bridging oxygen atoms. The $[\delta\text{-}Mo_8O_{26}]^{4-}$ polyoxoanion is similar to the $[\alpha\text{-}Mo_8O_{26}]^{4-}$ polyoxoanion. It is constructed from the edge and corner sharing of four $\{MoO_6\}$ octahedra and four $\{MoO_4\}$ tetrahedra. The overall cluster geometry may be described as a Mo_6O_6 equatorial ring capped on both poles by $\{MoO_4\}$ tetrahedra. The ring is composed of two pairs of edge-sharing octahedra linked by two tetrahedra via corner-sharing interactions (Figure S2).[9h] The Cu1 atom is three coordinated and shows a T-shaped coordination geometry that is surrounded by two N atoms from different bbi ligands and one terminal O atom from the $[\delta\text{-}Mo_8O_{26}]^{4-}$ anion. The Cu2, Cu3, and Cu4 atoms adopt close to linear coordination geometries, which are completed by two nitrogen atoms from different bbi ligands. Two kinds of bbi ligands link Cu1 and Cu2 atoms to generate an infinite chain that extends to a neutral double-chain $[Cu_2(bbi)_2(\delta\text{-}Mo_8O_{26})_{0.5}]^\infty$ by terminal oxygen atoms from the $[\delta\text{-}Mo_8O_{26}]^{4-}$ anion coordinating to two Cu1 atoms from different chains. Each isolated $[\alpha\text{-}Mo_8O_{26}]^{4-}$ polyoxoanion acts as a counterion. In addition, four terminal oxygen atoms from one $[\alpha\text{-}Mo_8O_{26}]^{4-}$ polyoxoanion link four Cu^I ions (two Cu2 and two Cu3) through strong Cu−O interactions with Cu−O distances of 2.806 Å for Cu3−O15 and 2.878 Å for Cu2−O20, respectively. In other words, each $[\alpha\text{-}Mo_8O_{26}]^{4-}$ polyanion links two Cu2 ions from the same double chain and two Cu3 ions from two adjacent single chains to generate an interesting 2-D sheet (Figures S3 and S4). Furthermore, each chain formed by Cu4 and the bbi ligand penetrates the 2-D sheet in an inclined way along the

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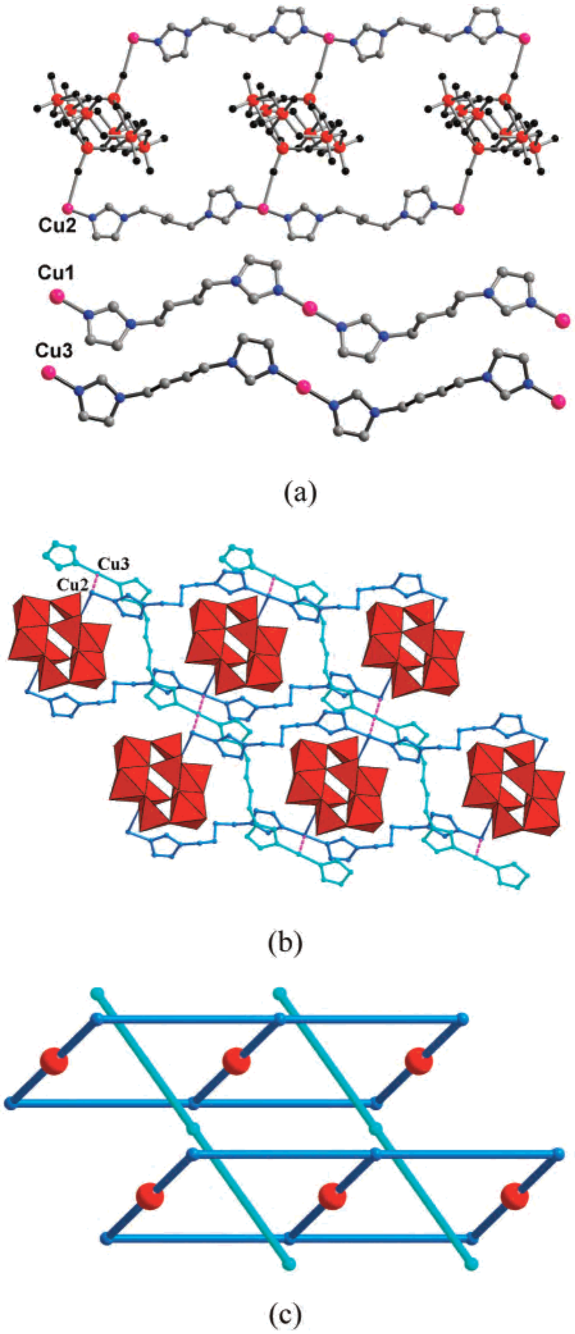
crystallographic *b*-axis to form the polythreaded structure (Figure 1b,c).[5] Furthermore, the distances of [Cu(1)−Cu(4)] and [Cu(2)−Cu(4)] are 3.227 and 3.185 Å, respectively, and they are similar to the van der Waals radii (2.8 Å) of Cu^I−Cu^I, which reveals the occurrence of cuprophilic interaction (Figure 1b).[15] The polythreaded structure extends to an intricate 3-D supramolecular structure by weak cuprophilic interaction (Figure 3a). To our knowledge, only one octamolybdate compound that contains two isomers (α and *β*) in the same crystal has been reported by us;[10] **1** represents the new example of a 3-D supramolecular structure that contains both α- and *δ*-octamolybdates.

Structural Description of 2. Compound **2** is composed of three kinds of subunits (Figure 2a). The crystallographic studies reveal that **2** contains three kinds of distinct copper(I) atoms, three kinds of bbi ligands, and one $[\theta\text{-}Mo_8O_{26}]^{4-}$ cluster.[9d] The structure of the $[\theta\text{-}Mo_8O_{26}]^{4-}$ polyanion may be described as a ring of four $\{MoO_6\}$ octahedra and two $\{MoO_5\}$ square pyramids in an edge- and corner-sharing arrangement, capped on either face by tetrahedral $\{MoO_4\}$ subunits in a corner-sharing mode. The ring is constructed of pairs of edge-sharing octahedra linked through the square pyramidal sites. Each square pyramids edge shares with one binuclear unit of octahedra and corner shares with the second (Figure S2). Cu1 and Cu3 display similar linear coordination geometries, which are completed by two N atoms from different bbi ligands. Cu2 is coordinated by two N atoms from distinct bbi ligands (Cu2-N) and one terminal oxygen atom (Cu2-O) from $[\theta\text{-}Mo_8O_{26}]^{4-}$, which exhibits a T-shaped coordination mode. The $[\theta\text{-}Mo_8O_{26}]^{4-}$ polyoxoanions pillar two adjacent Cu2-bbi monochains to generate a ladder-like double chain along the crystallographic *c*-axis. Furthermore, each chain formed by Cu3 penetrates the ladder-like double-chain in an inclined way to form the polythreaded structure (Figure 2b,c).[5] Each Cu2 atom has a weak cuprophilic interaction[15] with two Cu3 atoms in the distinct double chain with a Cu2···Cu3 distance of 3.229 Å. As a result, the ladder-like double chain extends to a 2-D supramolecular sheet (Figure 2b). The other chains, which are formed by Cu1 and bbi ligands and parallel to the ladder-like double chain, fill in the space between the two previously mentioned 2-D sheets (Figures 3b and S5).

Two compounds are synthesized by using Cu^{2+} ions, $(Mo_7O_{24})^{6-}$ polyanions, bbi ligands, and Et_3N. In **1** and **2**, the presence of Cu^I ions indicates that the starting Cu^{2+} ions are reduced, in a similar manner to previous investigations of in situ hydrothermal reactions.[16] The Cu^{2+} cations are easily reduced to Cu^+ cations by organic or inorganic nitrogenous compounds under hydrothermal conditions.[16] In this case, the starting Cu^{2+} ions are reduced to Cu^+, which may be due to the simultaneous presence of Et_3N and bbi ligands under hydrothermal conditions. Offering further insight into the nature of the reaction process, since the coordination ability of the nitrogen atoms from bbi ligands is stronger than water molecules and molybdate anions,[17] each Cu^+ cation is first coordinated by nitrogen atoms to form the $[Cu(bbi)^+]_n$ unit. Simultaneously, various octamolybdate isomers aggregate from $(Mo_7O_{24})^{6-}$ polyanions via changing pH values.[10,11] Then, the $[Cu(bbi)^+]_n$ compositions



(a)

(b)

(c)

Figure 2. (a) Ball-and-stick representation of three kinds of subunits: $[Cu(bbi)(\theta\text{-}Mo_8O_{26})_{0.5}]^-_\infty$ and two kinds of $[Cu(bbi)]^+_\infty$ coordination polymeric compositions. (b) Ball-and-stick and polyhedral representations of the 2-D polythreaded structure in **2**. (Red polyhedra represent $[\theta\text{-}Mo_8O_{26}]^{4-}$ polyoxoanions, and pink dashed lines represent Cu^I−Cu^I interactions between two $[Cu(bbi)]^+_\infty$ chains.) (c) Schematic representation of the polythreaded structure in **2**. (Red balls represent $[\theta\text{-}Mo_8O_{26}]^{4-}$ polyoxoanions, and cyan pillars represent $[Cu_3(bbi)]^+_\infty$ chains.)

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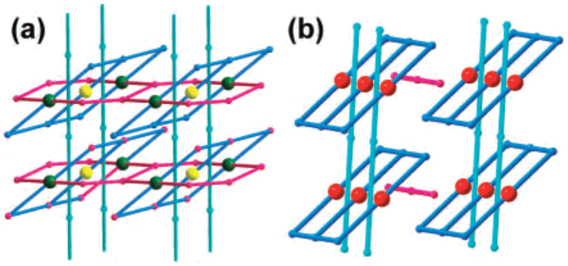

Figure 3. (a and b) Schematic representations of the supramolecular network of **1** and **2**. (Yellow, green, and red balls represent $[\delta\text{-}Mo_8O_{26}]^{4-}$, $[\alpha\text{-}Mo_8O_{26}]^{4-}$, and $[\theta\text{-}Mo_8O_{26}]^{4-}$ polyoxoanions, respectively.)

and $[Mo_8O_{26}]^{4-}$ isomers in the solution are assembled to ladder-like double chains through covalent linkages. The other $[Cu(bbi)^+]_n$ units pass through or are parallel to the double chains via Cu−O or cuprophilic interactions[15] to form the final products. In the formation process of **1** and **2**, two forces dominate the solution: one is the aggregation of octamolybdate isomers, and the other is the assembly of copper cations and bbi ligands into $[Cu(bbi)^+]_n$ chains. Then, nonbonding interactions, such as Cu−O and cuprophilic interactions, play crucial roles in the crystallization of isomers **1** and **2**.

According to previous literature by Müller and co-workers, the polymeric isopolyoxomolybdate species can possibly coexist in aqueous solution.[18] Direct crystallographic evidence, showing the coexistence of both $[Mo_6O_{19}]^{2-}$ and $[Mo_8O_{26}]^{4-}$ anions in the same crystal, has been found by Zubieta and others.[9f,11b,c] They considered that there exists an equilibrium shift between thermodynamic and kinetic domains in hydrothermal conditions, such that the equilibrium phases are replaced by structurally more complex metastable phases.[9f] Our group has reported one compound that contains two forms of octamolybdates: the α- and β-isomers.[10] Comparing the structures of **1** and **2**, there is one octamolybdate (θ-isomer) in **2**, while two kinds of octamolybdates (α-and δ-isomers) are exhibited in **1**. The coexistence of both the α-isomer and the δ-isomer of octamolybdate in **1** is an interesting phenomenon, which provides strong evidence for this study. The structure of the θ-isomer is clearly related to that of the α- and δ-isomers by the breaking of two bonds and the making of two bonds, respectively (Figure S2).[9d] If the θ-isomer is present instead of the α- and δ-isomers, **1** exhibits a similar structural type as **2**. The difference between **1** and **2** arises essentially from the octamolybdate isomers. The octamolybdate isomers may play a crucial role in the formation of supramolecular isomerism.

To date, supramolecular isomerism with a polythreaded topology has not been observed, while polyoxometalate compounds with a polythreaded topology are scarce.[19] Our work attempted to combine supramolecular isomerism, polythreading, and polyoxometalates, which are three important research fields. According to mathematical concepts, **1** and **2** are new types of compounds that are part of the intersection of the previously mentioned three research fields. This type of compound will further facilitate the exploration of new types of multifunctional materials with various properties.

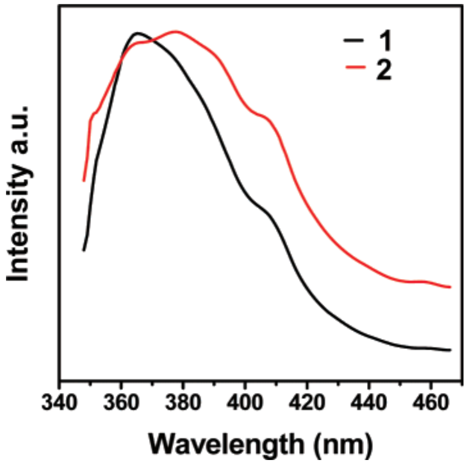

Figure 4. Emission spectra of **1** and **2** in the solid state at room temperature.

Luminescent Properties. The photoluminescence properties of **1** and **2** were studied at room temperature and are shown in Figure 4. It can be observed that the maximum emission wavelength occurs at 364 nm ($\lambda_{ex} = 300$ nm) for **1** and 377 nm for **2** ($\lambda_{ex} = 300$ nm), which are blue-shifted as compared to that of the pure bbi ligand ($\lambda_{em} = 438$ nm and $\lambda_{ex} = 300$ nm).[20] The origin of the emission for **1** might be attributable to ligand-to-metal (Cu^I) charge transfer and the intraligand $\pi^* \rightarrow \pi$ transitions of the neutral ligand.[21]

Conclusion

In conclusion, changing the reaction pH value may obtain various octamolybdate isomers that play a crucial role in the formation of supramolecular isomers **1** and **2**. Our research represents a new type of supramolecular isomerism with a polythreaded topology based on octamolybdate building blocks. The successful preparation of **1** and **2** may provide a calculable clue for supramolecular isomerism. Further research is ongoing to prepare novel supramolecular isomerism and to explore its valuable properties. More importantly, the combination of these three important research fields, namely, supramolecular isomerism, polythreaded systems, and polyoxometalate chemistry, opens up new possibilities in pursuit of multifunctional materials.

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Acknowledgment. We are thankful for financial support from the Program for Changjiang Scholars and Innovative Research Team in University, the National Natural Science Foundation of China (20573016), and the Science Foundation for Young Teachers of Northeast Normal University (20070309).

Supporting Information Available: Crystallographic data (CIF) and synthetic procedures, additional figures, and TGA spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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