



# Layered and molecular-structural control in polyoxomolybdate hybrid crystals by surfactant chain length

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## ABSTRACT

Polyoxomolybdate-surfactant hybrid layered crystals were synthesized by using single-tailed alkyl-trimethylammonium ( $[\text{C}_n\text{H}_{2n+1}\text{N}(\text{CH}_3)_3]^+$  ( $\text{C}_n$ ),  $n = 8, 10, 12, 14, 16$ , and  $18$ ) cations. The crystal structures consisted of alternate stacking of octamolybdate ( $[\text{Mo}_8\text{O}_{26}]^{4-}$ ,  $\text{Mo}_8$ ) anionic layers and surfactant cationic layers. The layered distance of the hybrid crystals became longer from 18.5 Å to 26.5 Å with an increase in alkyl chain length. Interestingly, the molecular structures of  $\text{Mo}_8$ , which has several isomers, depended on the alkyl chain length of the employed surfactants. Shorter surfactant ( $\text{C}_8$  and  $\text{C}_{10}$ ) formed hybrid crystals containing  $\beta$ -type  $\text{Mo}_8$  isomer, while surfactant with longer alkyl chain ( $\text{C}_{12}$ ,  $\text{C}_{14}$ ,  $\text{C}_{16}$ , and  $\text{C}_{18}$ ) gave crystals containing  $\delta$ -type  $\text{Mo}_8$  isomer. This structural controllability will lead to the precise functional control in the polyoxomolybdate-surfactant hybrid layered crystals.

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## 1. Introduction

Inorganic–organic hybrid materials [1–3] are more structurally controllable than purely inorganic compounds owing to organic components, and have potential for the construction of functionalized crystalline materials such as molecular conductors [4,5]. Polyoxometalate (POM) cluster anions are promising candidates as inorganic components due to their various physicochemical properties [6–10]. POMs can be organized by structure-directing surfactants to construct inorganic–organic hybrid materials [11–22] and layered crystals [23–36]. These POM-surfactant hybrids can allow fine tuning of the structure and function by changing the combination of POM anion and surfactant cation. The POM-surfactant hybrids have been assembled into crystalline [11,14], polymerized [12], and thin film [13] state. Several applications such as gas-sorption [11], photoluminescence [12], magnetic [13], and electrochemical [14] properties have been reviewed.

On the selection of POM anion, octamolybdate ( $[\text{Mo}_8\text{O}_{26}]^{4-}$ ,  $\text{Mo}_8$ ) is a popular species. However,  $\text{Mo}_8$  has several isomers such as  $\alpha$ -,  $\beta$ -,  $\gamma$ -, or  $\delta$ -type (Fig. 1) [37–41], and the type of isomers

affects the formulae and structures of the  $\text{Mo}_8$  crystals hybridized with surfactant [26–28]. For example, hexadecylpyridinium ( $[\text{C}_{16}\text{H}_{33}\text{N}(\text{C}_{16}\text{H}_{33})]^+$ ,  $\text{C}_{16}\text{py}$ ) cation forms several hybrid crystals with  $\text{Mo}_8$ . The  $\alpha$ - $\text{Mo}_8$  anion forms the crystal of  $(\text{C}_{16}\text{py})_4(\alpha\text{-Mo}_8)$ , where the counter cations are four  $\text{C}_{16}\text{py}$  per  $\alpha\text{-Mo}_8$  of 4- charge [26]. On the other hand,  $\beta$ - $\text{Mo}_8$  crystallizes with different number of  $\text{C}_{16}\text{py}$  to obtain  $(\text{C}_{16}\text{py})_3\text{Na}(\beta\text{-Mo}_8)$  [26] or  $(\text{C}_{16}\text{py})_2\text{H}_2(\beta\text{-Mo}_8)$  [27], and such introduction of small cations is interesting for the emergence of ionic or proton conductivity. Therefore, the precise control of the  $\text{Mo}_8$  isomer structure is crucial for constructing functional POM-surfactant hybrid crystals.

We report here syntheses and structures of hybrid layered crystal by using  $\text{Mo}_8$  and alkyltrimethylammonium,  $[\text{C}_n\text{H}_{2n+1}\text{N}(\text{CH}_3)_3]^+$  ( $\text{C}_n$ ,  $n = 8, 10, 12, 14, 16$ , and  $18$ ). The obtained crystals comprised different layered distance and the molecular structure of the  $\text{Mo}_8$  anion depending on the alkyl chain length of the  $\text{C}_n$  surfactants.

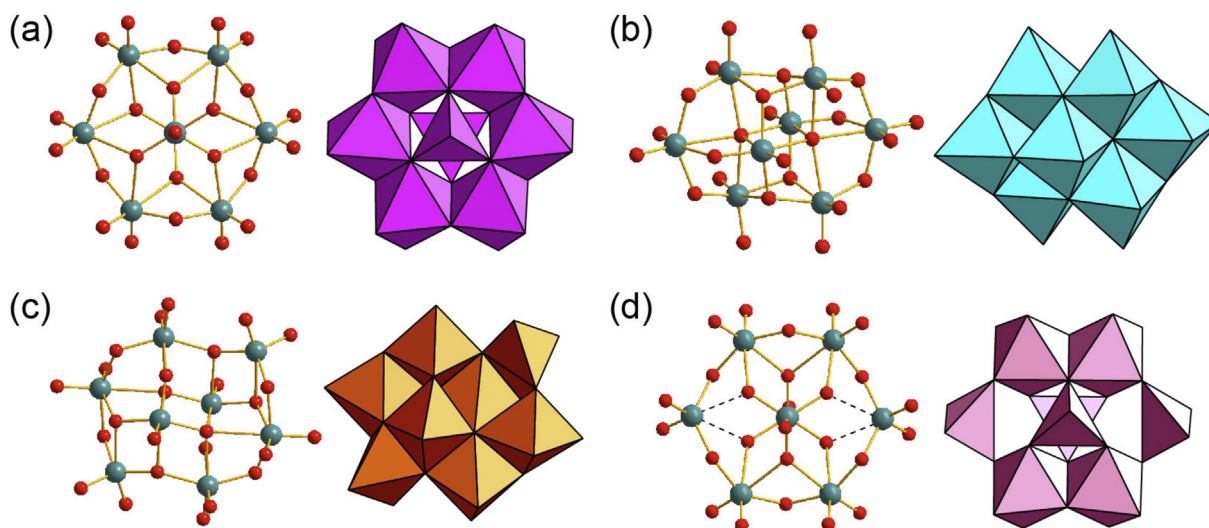
## 2. Experimental

### 2.1. Materials and general methods

All chemical reagents were obtained from commercial sources

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**Fig. 1.** Octamolybdate ( $\text{Mo}_8$ ) isomers in ball and stick (green: Mo, red: O) and polyhedral representations. (a)  $\alpha$ -, (b)  $\beta$ -, (c)  $\gamma$ -, and (d)  $\delta$ -type. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Wako and TCI, the highest grade) and employed without further purification. IR spectra (as KBr pellet) were recorded on a Jasco FT/IR-4200ST spectrometer. Powder X-ray diffraction (XRD) patterns were measured with a Rigaku MiniFlex300 and a Bruker AXS D8 ADVANCE diffractometers by using Cu  $K\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) at ambient temperature.

## 2.2. Syntheses of compounds

### 2.2.1. $\text{C}_8\text{-Mo}_8$ (**1**)

As cationic surfactant, octyltrimethylammonium bromide ( $[\text{C}_8\text{H}_{17}\text{N}(\text{CH}_3)_3]\text{Br}$ ,  $\text{C}_8\cdot\text{Br}$ ; TCI, purity > 98.0%) was employed.  $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$  (1.93 g, 8.0 mmol; Wako, purity > 99.0%) was dissolved in  $\text{H}_2\text{O}$  (10 mL), and the pH level was adjusted to 3.5–4.5 with 6 M HCl. To the acidified solution was added a water/ethanol (10 mL, 1:1 (v/v)) solution of  $\text{C}_8\cdot\text{Br}$  (0.76 g, 3.0 mmol), and stirred for 10 min. The resultant suspension was filtered, and obtained precipitates ( $\text{C}_8\text{-Mo}_8$ ) were dried in the air. Hot acetonitrile/ethanol (10 mL, 1:1 (v/v)) solution of the as-prepared  $\text{C}_8\text{-Mo}_8$  was kept at room temperature to give colorless plates of **1**. The crystals of **1** were efflorescent, and its elemental composition was calculated for the formula without a part of crystallization. Anal. Calcd for  $\text{C}_{46}\text{H}_{110}\text{N}_4\text{Mo}_8\text{O}_{27}$ : C, 28.79; H, 5.78; N, 2.92%. Found: C, 28.62; H, 5.38; N, 2.79%. IR (KBr disk): 941 (s), 913 (s), 876 (s), 833 (s), 715 (s), 670 (m), 564 (w), 524 (w), 507 (w), 458 (w)  $\text{cm}^{-1}$ .

### 2.2.2. $\text{C}_{10}\text{-Mo}_8$ (**2**)

Colorless plates of **2** were obtained by a similar procedure for **1**. As cationic surfactant, decyltrimethylammonium bromide ( $[\text{C}_{10}\text{H}_{21}\text{N}(\text{CH}_3)_3]\text{Br}$ ,  $\text{C}_{10}\cdot\text{Br}$ ; TCI, purity > 99.0%) was used instead of  $\text{C}_8\cdot\text{Br}$ . The crystals of **2** were efflorescent, and its elemental composition was calculated for the formula without solvent of crystallization. Anal. Calcd for  $\text{C}_{52}\text{H}_{120}\text{N}_4\text{Mo}_8\text{O}_{26}$ : C, 31.46; H, 6.09; N, 2.82%. Found: C, 31.32; H, 5.81; N, 2.83%. IR (KBr disk): 943 (s), 915 (s), 859 (m), 787 (w), 753 (w), 718 (m), 667 (m), 637 (w), 580 (w), 546 (w), 519 (w), 482 (w), 458 (w), 458 (w), 442 (w), 412 (w)  $\text{cm}^{-1}$ .

### 2.2.3. $\text{C}_{12}\text{-Mo}_8$ (**3**)

Colorless crude product of  $\text{C}_{12}\text{-Mo}_8$  hybrid was obtained by a similar procedure for the as-prepared  $\text{C}_8\text{-Mo}_8$  hybrid. Dodecyltrimethylammonium chloride ( $[\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3]\text{Cl}$ ,  $\text{C}_{12}\cdot\text{Cl}$ ; Wako,

purity > 97.0%) was used instead of  $\text{C}_8\cdot\text{Br}$ . Colorless plates of **3** were obtained by recrystallization of the as-prepared  $\text{C}_{12}\text{-Mo}_8$  hybrid by hot acetonitrile. Anal. Calcd for  $\text{C}_{60}\text{H}_{134}\text{N}_4\text{Mo}_8\text{O}_{26}$ : C, 34.36; H, 6.54; N, 2.67%. Found: C, 34.32; H, 6.38; N, 2.71%. IR (KBr disk): 943 (m), 916 (s), 858 (m), 805 (m), 718 (w), 668 (m), 557 (w), 517 (w)  $\text{cm}^{-1}$ .

### 2.2.4. $\text{C}_{14}\text{-Mo}_8$ (**4**)

Colorless plates of **4** were obtained was obtained by a similar procedure for **3**. Tetradecyltrimethylammonium bromide ( $[\text{C}_{14}\text{H}_{29}\text{N}(\text{CH}_3)_3]\text{Br}$ ,  $\text{C}_{14}\cdot\text{Br}$ ; TCI, purity > 98.0%) was used instead of  $\text{C}_{12}\cdot\text{Cl}$ . Anal. Calcd for  $\text{C}_{68}\text{H}_{152}\text{N}_4\text{Mo}_8\text{O}_{26}$ : C, 36.97; H, 6.93; N, 2.54%. Found: C, 36.57; H, 6.81; N, 2.50%. IR (KBr disk): 953 (m), 915 (s), 858 (m), 806 (s), 720 (w), 666 (m), 553 (w), 518 (w)  $\text{cm}^{-1}$ .

### 2.2.5. $\text{C}_{16}\text{-Mo}_8$ (**5**)

Colorless plates of **5** were obtained was obtained by a similar procedure for **3**. Hexadecyltrimethylammonium bromide ( $[\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]\text{Br}$ ,  $\text{C}_{16}\cdot\text{Br}$ ; Wako, purity > 98.0%) was used instead of  $\text{C}_{12}\cdot\text{Cl}$ . Anal. Calcd for  $\text{C}_{76}\text{H}_{168}\text{N}_4\text{Mo}_8\text{O}_{26}$ : C, 39.32; H, 7.29; N, 2.41%. Found: C, 38.52; H, 7.29; N, 2.32%. IR (KBr disk): 952 (m), 916 (s), 858 (m), 804 (s), 720 (w), 666 (m), 554 (w), 518 (m)  $\text{cm}^{-1}$ .

### 2.2.6. $\text{C}_{18}\text{-Mo}_8$ (**6**)

Colorless plates of **6** were obtained was obtained by a similar procedure for **3**. Octadecyltrimethylammonium chloride ( $[\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3]\text{Cl}$ ,  $\text{C}_{18}\cdot\text{Cl}$ ; TCI, purity > 97.0%) was used instead of  $\text{C}_{12}\cdot\text{Cl}$ . Anal. Calcd for  $\text{C}_{84}\text{H}_{184}\text{N}_4\text{Mo}_8\text{O}_{26}$ : C, 41.45; H, 7.62; N, 2.30%. Found: C, 41.27; H, 7.33; N, 2.38%. IR (KBr disk): 953 (m), 916 (s), 858 (m), 816 (s), 721 (w), 665 (m), 550 (w)  $\text{cm}^{-1}$ .

## 2.3. Crystal structure determination

Single crystal X-ray diffraction measurements were performed on a Rigaku RAXIS RAPID imaging plate diffractometer with graphite monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71075 \text{ \AA}$ ). The diffraction measurements for **5** were also carried out with a Rigaku VariMax with RAPID diffractometer using Mo- $K\alpha$  radiation. Diffraction data were collected and processed with PROCESS-AUTO [42]. The structures were solved by direct methods (SHELXS97 [43] or SIR92 [44]) for **1**, **2**, **5**, and **6**, and by heavy-atom Patterson methods (PATTY [45]) for **3** and **4**, and expanded using Fourier techniques. The refinement procedure was performed by the full-

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